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THE CONDUCTANCES OF AQUEOUS SOLUTIONS OF SULPHURIC ACID AT 50° AND 75°[1]

BY A. N. CAMPBELL, E. M. KARTZMARK, D. BISSET, AND M. E. BEDNAS[2]

ABSTRACT

The specific and equivalent conductances of aqueous solutions of sulphuric acid, ranging in concentration from 5 to 95% by weight, have been determined, as well as the densities and viscosities.

The data on the conductance of sulphuric acid available in the literature refer to temperatures of 18° (4) and 25°, 60°, and 95° C. (5). With the exception of 18° these data have only recently appeared and for them an accuracy not greater than 1% is claimed. The author of the work, Roughton, did not determine densities, so that it is impossible to calculate equivalent conductances from his work.

The present work had no theoretical aim and has no connection with our work on strong salt solutions (3). Sulphuric acid has almost zero conductance in the anhydrous state, a behavior characteristic of acids. This means that the mechanism of ionization is fundamentally different from that of salts and therefore cannot be given the same theoretical treatment.

EXPERIMENTAL

Our technique has already been described (3); it yields an accuracy of 0.1% in the conductance measurements; densities are good to five significant figures; viscosities and fluidities are good to four. Viscosities were determined in Ostwald-Fenske viscometers; they were calibrated with water for solutions of lower viscosity and with sucrose solutions for higher viscosities, as described by Bingham and Jackson (1). The temperature variations of the thermostats were: at 50°, ± 0.01°, at 75° ± 0.02°. The concentrations were determined both volumetrically and gravimetrically as barium sulphate, with an accuracy of 0.1%.

RESULTS

The results of the measurements are contained in Table I.

[1] *Manuscript received October 23, 1952.*
Contribution from the Chemistry Department of the University of Manitoba, Winnipeg, Man.

[2] *Holder of National Research Council Bursary.*

TABLE I

THE SPECIFIC AND EQUIVALENT CONDUCTANCES, DENSITIES, VISCOSITIES, AND FLUIDITIES OF AQUEOUS SOLUTIONS OF SULPHURIC ACID AT 50° AND 75° C.

Wt. %	Normality	Density, gm./ml.	Specific conductance, mhos	Equivalent conductance, mhos	Viscosity, centipoises	Fluidity, rhes
A. 50° C.						
5.66	—	—	0.3058	—	—	—
8.95	1.870	1.0449	0.4901	262.1	0.5802	172.4
10.53	—	—	0.5714	—	—	—
17.11	3.76	1.1002	0.8377	222.8	0.7828	127.7
21.38	—	—	0.9767	—	—	—
24.15	5.56	1.1519	1.0338	185.9	0.9355	106.9
30.85	7.44	1.2049	1.1117	149.4	1.1230	89.05
31.76	—	—	1.1234	—	—	—
36.30	—	—	1.1133	—	—	—
41.12	—	—	1.0725	—	—	—
43.45	11.40	1.3111	1.0258	90.0	1.6712	59.88
52.15	—	—	0.8532	—	—	—
53.12	14.90	1.4021	0.8169	54.82	2.3498	42.56
55.74	15.92	1.4295	0.7541	47.42	2.642	37.85
60.45	17.76	1.4686	0.6616	37.25	3.076	32.51
61.04	—	—	0.6364	—	—	—
67.65	21.86	1.5566	0.4642	22.04	4.467	28.57
72.62	23.44	1.6138	0.3620	15.44	5.891	16.98
75.41	24.82	1.6461	0.3125	12.59	6.868	14.56
78.70	—	—	0.2729	—	—	—
82.95	28.66	1.7273	0.2403	8.385	9.543	10.48
87.13	—	—	0.2347	—	—	—
89.99	—	—	0.2330	—	—	—
92.8	33.36	1.7973	0.2285	6.850	9.696	10.31
96.2	34.76	1.8065	0.1782	5.127	9.952	10.05
B. 75° C.						
5.66	—	—	0.3442	—	—	—
8.95	1.848	1.0328	0.5608	303.5	0.3893	2.186
10.53	—	—	0.6345	—	—	—
17.11	3.74	1.0963	0.9791	261.8	0.4575	1.809
21.38	—	—	1.1449	—	—	—
24.15	5.50	1.1378	1.2351	224.6	0.5527	1.545
30.85	7.34	1.1903	1.3647	185.9	0.5529	1.282
31.76	—	—	1.3747	—	—	—
36.30	—	—	1.3869	—	—	—
37.53	9.34	1.2435	1.3827	148.0	0.7799	1.051
41.12	—	—	1.3566	—	—	—
43.45	11.24	1.2940	1.3127	116.8	0.9515	0.8717
52.15	—	—	1.1349	—	—	—
53.12	14.72	1.3859	1.1143	75.70	1.1471	0.6190
55.74	15.74	1.4126	1.0035	63.75	1.794	0.5583
60.45	17.52	1.4492	0.8915	50.88	1.791	0.4821
61.04	—	—	0.8670	—	—	—
67.65	20.82	1.5384	0.6594	31.67	2.074	0.4599
72.62	23.14	1.5926	0.5337	23.06	2.975	0.2693
75.41	24.54	1.6266	0.4764	19.34	3.713	0.2411
78.70	—	—	0.4290	—	—	—
82.95	28.30	1.7061	0.3877	13.70	4.148	0.1872
87.13	—	—	0.3699	—	—	—
89.99	—	—	0.3558	—	—	—
92.80	32.98	1.7767	0.3456	10.48	5.341	0.1765
96.20	34.38	1.7872	0.2641	7.68	5.666 5.849	0.1710

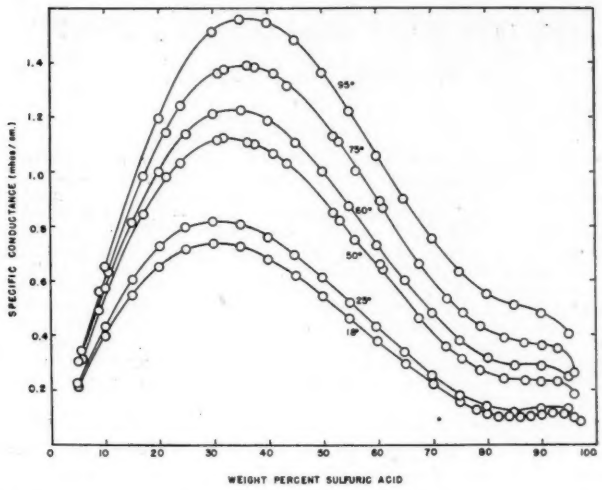

FIG 1. Specific conductance of aqueous sulphuric acid solutions as a function of concentration and temperature.

DISCUSSION

In the graph (Fig. 1) specific conductance is plotted against weight per cent sulphuric acid, not only for the temperatures of this paper but for 18°, 25°, 60°, and 95°, the latter figures being taken from the literature previously given. All the curves are similar in character in so far as they exhibit a pronounced maximum between 30 and 35% sulphuric acid. A second maximum, much less pronounced, is observed in the lower temperature curves. The graphs show that the first maximum becomes sharper with rising temperature and its composition shifts a little in the direction of higher sulphuric acid content, while the second maximum gets flatter and has disappeared entirely at 75°.

In our work on silver nitrate and ammonium nitrate (2) we have noticed a remarkable degree of constancy in the ratio of the mean temperature coefficient of fluidity to that of conductance, but no such constancy is found here.

ACKNOWLEDGMENT

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THE ELECTRODE BEHAVIOR OF MERCURY[1]

By A. K. Wiebe and C. A. Winkler

ABSTRACT

Mercury electrode potentials in $N/5$ sulphuric acid were unaffected when the electrolyte was saturated with hydrogen, nitrogen, or helium but were markedly affected by trace amounts of oxygen or mercury ions. In the absence of oxygen and mercury ions, a constant potential of -0.61 volt (relative to a saturated calomel electrode) was observed. When current was passed for the first time across a fresh electrode face immersed in oxygen-free electrolyte (i.e. from initial potentials of about -0.61 volt), the potential build-up was nonlinear, but subsequent passage of current gave a linear build-up of potential. With traces of oxygen present, differences in the two types of curves were masked by reactions that appeared to involve oxygen or oxide on the electrode surface. The initial build-up curve was ascribed to the deposition of a monatomic hydrogen film (one atom per metal atom in the surface). The potential build-up curves probably result from a number of simultaneous reactions at the electrode.

From recent studies in this laboratory (15) with copper and silver cathodes immersed in sulphuric acid, it was tentatively concluded that measurement of surface areas by the Bowden–Rideal method (8) depends on the rate of charging a condenser at the surface, as distinct from the rate of increase of hydrogen overvoltage, which appeared to be associated with the deposition of a layer of hydrogen on the cathode.

Similar experiments with mercury cathodes have yielded the results recorded in the present paper.

EXPERIMENTAL AND RESULTS

The cathode ray oscillograph unit and Leeds and Northrup type K potentiometer arrangement were identical with those described in earlier papers (12, 13).

The electrolytic cell, shown in Fig. 1, was provided with a glass cup of 2.20 cm. internal diameter to contain the mercury cathode. The height of the meniscus, measured under experimental conditions with a cathetometer, was 2.23 ± 0.05 mm. Assuming the meniscus to be spherical, and the contact angle of mercury on wet glass to be 140° (1), the area of the mercury surface was estimated to be 4.3 cm.^{2} Since the cross-sectional area of the cup was 3.8 cm.^{2}, the correction applied for the meniscus was about 12% of the total area. Hence, even assuming a liberal error of 10–20% in the correction, the corrected area should not be in error by more than 1–2%.

All glassware, including the cell, was washed once with chromic acid, three times with alcoholic potassium hydroxide, several times with twice distilled water, and finally steamed out for several hours using twice distilled water in the steam generator.

Hydrogen was purified by the method described in a previous paper (12). Nitrogen and helium were freed from oxygen by passing them through a Pyrex glass tube packed with elemental copper and maintained at a tempera-

[1] *Manuscript received August 15, 1952.*
Contribution from the physical chemistry laboratory, McGill University, Montreal, Que., with financial assistance from the National Research Council.

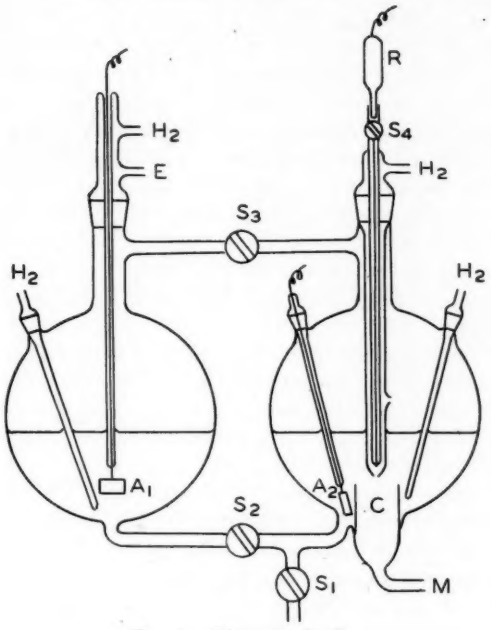

FIG. 1. Diagram of cell.

ture of 400°–450° C. The copper was a porous form obtained by reducing copper oxide wire with electrolytic tank hydrogen. All gases were passed through a potassium hydroxide bubbler before they reached the cell.

The $N/5$ sulphuric acid was made with twice distilled water and distilled reagent grade sulphuric acid. The solution was outgassed under reduced pressure for 24–48 hr., and stored under hydrogen, nitrogen, or helium. It was introduced into the electrolytic cell through "Tygon" (plastic) tubing.

Mercury was purified by first drawing air through the hot (300° C.) liquid for 12 hr., after which it was dropped from a capillary tip three times through each of the following solutions: alcoholic potassium hydroxide (10%), aqueous potassium hydroxide (10%), aqueous nitric acid (10%), and twice distilled water. The mercury was then dried at 110° C., distilled under vacuum, and the distillate subjected to the complete purification treatment a second time. The dry mercury from the second treatment was stored under hydrogen or nitrogen and distilled in batches as required. The second purification produced no observable changes in electrode behavior.

The surface of the mercury cathode was renewed when desired by alternately overflowing mercury from the cup and dropping the level into the narrow tube leading from the cup to the outside of the cell.

All potential measurements were made in reference to a saturated calomel electrode.

The main object of this investigation was to study the potential changes

observed during the first few minutes of current flow (i.e. potential build-up curves). Some observations of potentials and potential changes on open circuit were also made, since it seemed possible that such information might aid in the interpretation of the potential build-up curves.

The initial potential on a fresh mercury surface became increasingly negative as oxygen was removed from the electrolyte ($N/5$ sulphuric acid) by electrolytic reduction at the mercury cathode (2, 8). Such potentials were not stable, however, and changed rapidly to more positive values unless the initial potential was of the order of -0.60 volt. As the initial potential approached this value, the rate of change of potential decreased until a nonvarying and reproducible potential of -0.617 ± 0.002 volt was obtained. (Such a steady-state potential may, for convenience, be termed a zero potential.) The zero potential was now unaffected when nitrogen was used in place of hydrogen to saturate the electrolyte or when the electrolyte was stirred by bubbling hydrogen or nitrogen. In future reference to oxygen-free electrolyte it should be understood that the electrolyte was treated as above until a steady potential of about -0.61 volt was obtained.

A reasonably constant potential of -0.605 ± 0.008 volt was generally obtainable after 15 to 20 hr. of pre-electrolysis but much longer periods were required when the system had become thoroughly contaminated with oxygen during a previous experiment. Since hydrogen overvoltage is quite strongly affected by trace quantities of many impurities (cf. 2, 5, 11), it seemed possible that the zero potential might similarly be due, not to the removal of oxygen from the electrolyte, but to some impurity such as sulphide ion, either present in trace amounts under all experimental conditions, or introduced by the prolonged periods of electrolysis.

To examine the possibility that the potential of -0.61 volt resulted from introduction of a trace impurity by the prolonged electrolysis, the anode compartment of the cell (Fig. 1) was rinsed and filled with $N/5$ sulphuric acid which had been previously outgassed under reduced pressure. A piece of platinum foil was rendered catalytically active for the hydrogen and oxygen reaction by alternately making it anodic and cathodic in sulphuric acid (6). It was then made anodic in the electrolyte and a small current (6×10^{-7} amp.) was passed for three hours while purified hydrogen was bubbled through the solution and around the activated anode. A renewed mercury surface had a steady zero potential of -0.599 volt after the cathode compartment had been rinsed and charged with the anodically treated electrolyte. This value may be compared with the potentials obtained after pre-electrolysis at a mercury cathode (i.e. -0.61 volt).

Since a substance (e.g. sulphide ion) cannot be introduced into a system by both cathodic reduction and anodic oxidation, it would seem reasonable to conclude that some potential-determining material, present in the original electrolyte, was capable of being removed either by electrolysis at a mercury cathode or by electrolysis at an activated platinum anode bathed in hydrogen. It is difficult to conceive of any substance other than oxygen that would behave in this manner.

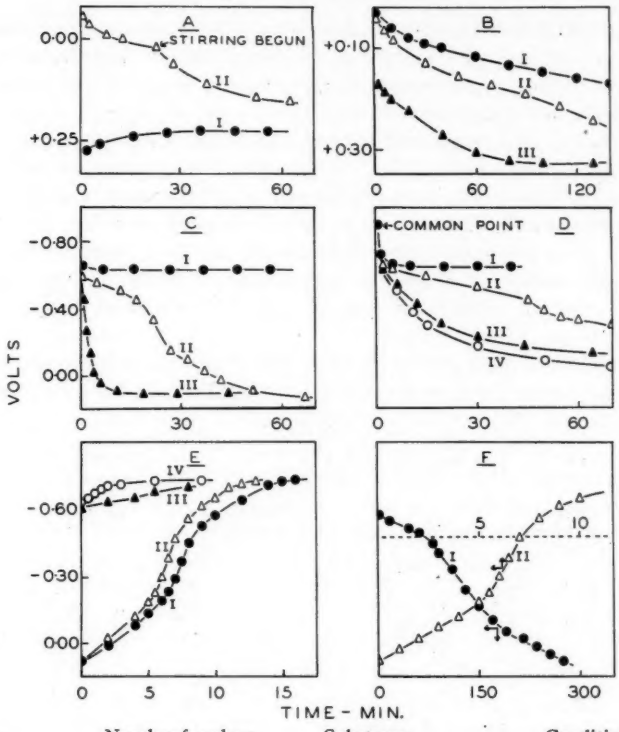

FIG. 2.

Curve	Number faradays passed	Substance introduced	Condition in electrolyte
A I	2.8×10^{-7}	Mercury ion	Oxygen free
II	2.8×10^{-7}	"	"
			(Mercury surface renewed)
B I	2.0×10^{-7}	Oxygen	N_2 saturated—stirred
II	3.0×10^{-6}	"	" "
III	1.0×10^{-5}	"	" "
C I	Nil	.....	N_2 saturated—stirred
II	2×10^{-9}	Oxygen	" "
III	2×10^{-9}	"	Helium " "
D I	Nil	.....	N_2 saturated—stirred
II	8.0×10^{-9}	Oxygen	" "
III	1.9×10^{-8}	"	" "
IV	5.6×10^{-8}	"	" "
E I	10^{-10}	Oxygen	(Fresh mercury surface)
II	10^{-10}	"	
III	Nil		(Fresh mercury surface)
IV	Nil		
F I	10^{-10}	Oxygen	Unstirred
II	10^{-10}	"	

The possibility that the potential value of -0.61 volt was due to traces of an impurity present in the electrolyte at all times would seem to be ruled out

by the fact that this potential value was attained almost immediately after the mercury surface was renewed in the deoxygenated electrolyte. With trace amounts of oxygen or mercury ions, potentials changed slowly over periods of one to five hours (Fig. 2, *A* and *B*).

The zero potential was found to be markedly affected by low concentrations of either oxygen or mercury ions. After these substances had been removed by pre-electrolysis until a reasonably constant potential of about −0.61 volt was obtained, small quantities of oxygen were evolved in nitrogen saturated electrolyte at a small auxiliary platinum anode (A_2 of Fig. 1), by passing a known small current for definite periods of time. Known quantities of mercury ions were similarly introduced with the mercury electrode now acting as an anode.

The amounts of mercury ion estimated to be introduced into the electrolyte in this way (Table I) represent upper limits. Processes other than solution of

TABLE I

THE EFFECT OF MERCURY IONS AND OXYGEN ON THE ZERO POTENTIAL

Number faradays passed to introduce mercury ion*	Potential, volt	Number faradays passed to introduce oxygen*	Potential, volt	
7.8×10^{-8}	−0.558	2×10^{-9}	+0.11	Approximate
2.0×10^{-7}	+0.120	2×10^{-8}	+0.16	
2.8×10^{-7}	+0.200	7.6×10^{-8}	+0.28	
4.0×10^{-7}	+0.280	2.0×10^{-7}	+0.326	
		4.0×10^{-6}	+0.326	
		1.0×10^{-4}	+0.334	After 20 hr.

**Expressed in terms of 1 liter of electrolyte.*

mercury ions during passage of current, or adsorption of mercury ions at the wall, would reduce the amounts present in solution by an unknown amount. Similar considerations apply to the amounts of oxygen in solution. Also, no account is taken here of the amount of oxygen that may be lost to the atmosphere above the solution. For these reasons, the relative amounts of mercury ions or oxygen in the electrolyte are expressed in terms of the number of faradays passed, rather than as actual concentration terms.

When quantities of oxygen calculated as sufficient to react with 2–3% of the cathode surface were introduced into the catholyte, the potential of a mercury surface changed from −0.61 volt to about +0.10 volt while the introduction of corresponding amounts of mercury ions had a negligible effect (Table I). This behavior would seem to eliminate the possibility that mercuric oxide formed on the cathode surface immediately dissolves and that the resulting mercury ions are the sole potential determining factor. When the current was switched off after evolving mercury ions at the mercury electrode, the final value of the potential was approached from the positive side (curve I, Fig. 2*A*). On now renewing the surface the same ultimate potential was approached from the negative side (curve II). This behavior would seem to indicate that mercury ions affect the potential by being adsorbed directly

onto the electrode surface and that an equilibrium exists between adsorbed ions and the concentrations of ions in solution.

The zero potential in oxygen-free electrolyte remained the same (within experimental error) in solutions saturated with hydrogen, nitrogen, or helium. Similarly, the ultimate value of the potential in the presence of small amounts of oxygen (up to the maximum amount in Table I) was the same in electrolyte saturated with either nitrogen or helium. However, the time required for the potential to reach its final value in electrolyte saturated with nitrogen, although varying with the amount of oxygen introduced (Fig. 2*B*), was always many times that required in electrolyte saturated with helium (Fig. 2*C*). The marked retarding effect of nitrogen on the rate of attainment of a stable potential in solutions containing oxygen indicates that nitrogen is strongly adsorbed on the mercury surface but that the forces of attraction between molecular nitrogen and surface mercury atoms are insufficient to affect the final value of the potential appreciably. It does not seem likely, therefore, that the large effect of trace quantities of oxygen on the mercury electrode potential can be explained on the basis of physical adsorption. The results appear to be more reasonably explained on the assumption that the potential of $+0.330 \pm 0.004$ volt, observed with larger amounts of oxygen, is to be associated with a monatomic layer of chemisorbed oxygen on the surface.

The electrode potential in $N/5$ sulphuric acid saturated with oxygen changed from an initial value of $+0.330$ volt to $+0.393$ volt in three hours. The potential then changed slowly at about 1 mv. per hr. to $+0.413$ volt when the experiment was discontinued. A value of $+0.40$ volt is generally accepted for the zero potential of a mercury cathode in oxygen saturated electrolyte (9). Potentials more positive than $+0.330$ volt may be due to the slow solution of mercuric oxide to form Hg^{++} ions. Much more study is required to clarify the relation between systems containing small traces of oxygen and those saturated with oxygen. However, the fact that the potential of $+0.41$ volt observed in oxygen-saturated electrolyte is the same as that for the mercury–mercurous sulphate electrode may be significant.

The presence of oxygen influences not only the zero potential at a mercury surface, but also alters the behavior of potential decay curves (Fig. 2*D*). These were obtained by allowing the potential to decay on open circuit after current had been passed until the maximum value of the overvoltage (about -0.90 volt) had been reached. In oxygen-free electrolyte, the potential decayed to -0.636 volt (curve I) which differed by about 20 mv. from the zero potential (-0.617 ± 0.002 volt) previously recorded under the same conditions. Small quantities of oxygen caused the potential to decay to more positive values and over longer periods of time (curves II, III, and IV).

Potential build-up curves, of which those in Fig. 2*E* are typical, also proved to be sensitive to the presence of oxygen. Curves I and III represented the initial potential build-up determined potentiometrically when current was made to flow for the first time across the face of a renewed mercury surface, while curves II and IV were obtained on the same surfaces as I and III and with identical current after allowing the potentials to decay, with the circuit

open, to their initial values. Curves III and IV represent the potential build-up behavior in oxygen-free electrolyte, while curves I and II show the effect of trace quantities of oxygen.

Initial potential build-up curves on a new surface could be reproduced only after the elapse of not less than 30 min. between the renewal of a mercury surface and the commencement of such a curve, since renewing the cathode surface unavoidably brought the mercury into a state of violent agitation. In all subsequent experiments, a minimum period of one hour was allowed for the mercury to come to rest after the surface was renewed before the current was switched on.

Potential build-up curves established from initial potentials in the neighborhood of +0.10 volt fell into three distinct sections (curves I and II, Fig. 2*E*). The initial build-up curve, as well as subsequent curves on the same surface, had linear sections of identical slope between −0.20 volt and −0.45 volt. This range of potential values is attained only in the presence of oxygen or mercury ions, in contrast with stable more negative values (*ca.* −0.61 volt) obtained in electrolyte free of oxygen and mercury ions. Hence, potential changes in the range −0.20 to −0.45 volt would seem to be the result of some reaction involving these substances. The rate of potential change for the linear section in this region measured over a current range (1.18×10^{-7} amp.–2.45×10^{-5} amp.) corresponded to a capacitance of 21 ± 2 microfarads per cm.^{2} in agreement with values found by other investigators (cf. 3, 7).

Like the potential build-up curve, the zero potential curve (curve I, Fig. 2*F*) exhibited three distinct sections with the breaks between the linear sections occurring at almost identical potentials in both curves. The potential build-up curve of Fig. 2*F* is a reproduction of a portion of curve II, Fig. 2*E*. The zero potential curve was obtained by introducing about 10^{-10} mole (10^{-9} mole per liter) of oxygen into an oxygen-free system after which the change of potential on a renewed mercury surface was observed potentiometrically. The solution was unstirred so that the process was diffusion controlled. If it may be assumed that the rate of diffusion of oxygen was approximately constant for the part of the reaction represented by the zero potential curve, then approximately equal quantities of oxygen would react with the cathode surface in equal increments of time. Hence, the fact that both curves have similar shapes would seem to indicate that, during current flow, chemisorbed oxygen is removed from the cathode surface at an approximately constant rate. The potential range −0.20 to −0.45 volt appears to correspond to some critical condition of the electrode surface when the potential is most sensitive to changes in the quantity of chemisorbed oxygen.

When initial potential build-up curves were established under oxygen-free conditions and in electrolyte containing trace amounts of oxygen, equal quantities of current were required to establish the maximum potential (Table III). However, with trace amounts of oxygen present, approximately half the total current was required to change the potential from +0.10 volt to the initial potential (−0.61 volt) of the build-up curve established in an oxygen-free system. An amount of chemisorbed oxygen involving not more

than a few per cent of the cathode surface has been shown to result in a potential of +0.10 volt. It would appear, then, that at low current densities, this oxygen is reduced with a very low current efficiency.

Potential build-up curves established on a mercury cathode from initial potentials of about −0.61 volt were of two distinct types. The initial build-up curves were nonlinear throughout as shown in curve III of Fig. 2*E*. In contrast, the subsequent build-up curves on the same surface were always linear but the slope varied with the time allowed for the potential to decay after current had been passed. After a period of decay of one minute the rate of build-up corresponded to an apparent capacitance of about 30 microcoulombs per volt cm.^{2} but as the time allowed for the potential to decay was increased, the subsequent rate of potential build-up on closing the circuit decreased to a limiting value corresponding to an apparent capacitance of 200 microcoulombs per volt cm.^{2} The limiting value of the rate of potential build-up was obtained when the circuit was closed after allowing the potential decay process to reach completion (curve I, Fig. 2*D*).

Potential build-up curves also yield useful information from the time required for the potential to reach a maximum, in particular as it applies to the initial potential build-up curves. For convenience, the time required to reach the maximum potential when current is made to flow for the first time across the face of a fresh mercury surface (i.e. the initial potential build-up curve) will be designated t_{max}. To determine t_{max}, a smooth curve was drawn through an open scale plot of the points representing the final 10 to 20 mv. of the potential change. The logarithms of the times for attainment of equal increments of potential in this region were plotted against the corresponding potential and the resultant approximately linear relation was extrapolated to the ordinate corresponding to the potential maximum. Some typical potential build-up curves, and a typical linear extrapolation to t_{max}, are shown in Fig. 3.

Determinations of t_{max} were made for a variety of experimental conditions

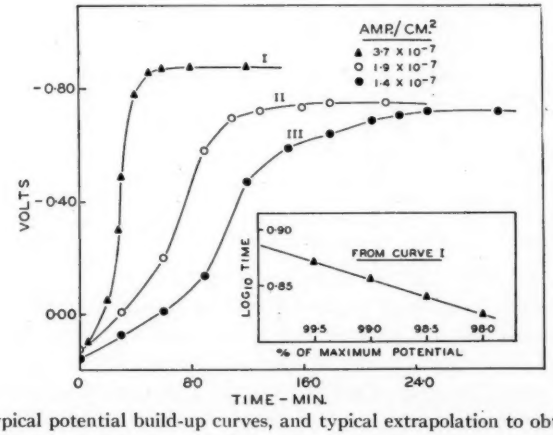

FIG. 3. Typical potential build-up curves, and typical extrapolation to obtain t_{max}.

such as varying the current in oxygen-free electrolyte (Table II), varying the initial potential at a given current (Table III), and varying the current in electrolyte which had not been pre-electrolyzed (Table IV). For the latter

TABLE II

TYPICAL VALUES OF It_{max} MEASURED AT VARIOUS CURRENTS IN O_2 FREE $N/5$ SULPHURIC ACID

Time of pre-electrolysis, hr.	Initial potential, volt	Current, amp.	It_{max}, microamp-min.	Dev'n. from It_{max} calculated, %
16	−0.605	5.40×10^{-7}	13.0	+ 5
17	−0.610	5.80×10^{-7}	11.6	− 6
19	−0.597	5.89×10^{-7}	13.1	+ 5
16	−0.600	8.22×10^{-7}	11.2	−10
40	−0.593	1.11×10^{-6}	12.6	+ 2
17	−0.601	2.08×10^{-6}	12.5	+ 1
15	−0.592	4.10×10^{-6}	11.9	− 4
17	−0.605	6.15×10^{-6}	12.3	− 1
Average			12.3	− 1

TABLE III

TYPICAL VALUES OF It_{max} WITH VARIATION OF THE INITIAL POTENTIAL

Initial potential, volt	Current, amp.	It_{max}, microamp-min.	Dev'n. from It_{max} calculated, %
−0.610	5.80×10^{-7}	13.1	+ 5
−0.557	5.48×10^{-7}	13.0	+ 5
−0.536	5.56×10^{-7}	12.8	+ 3
−0.401	5.92×10^{-7}	14.0	+13
−0.215	6.30×10^{-7}	13.6	+10
−0.008	6.46×10^{-7}	12.9	+ 4
+0.088	6.71×10^{-7}	14.1	+14

TABLE IV

TYPICAL VALUES OF It_{max} IN NON-PRE-ELECTROLYZED $N/5$ SULPHURIC ACID

Current, amp.	Initial potential, volt	It_{max}, microamp-min.	Dev'n. from It_{max} calculated, %
6.08×10^{-7}	0.16	14.2	+15
7.95×10^{-7}	0.12	14.0	+13
1.26×10^{-6}	0.11	13.2	+ 6
2.03×10^{-6}	0.15	12.0	− 4
3.81×10^{-6}	0.12	14.5	+17
6.07×10^{-6}	0.08	12.2	− 2

experiments the $N/5$ sulphuric acid was outgassed over a period of several days by alternately evacuating and saturating it with purified hydrogen. A piece of platinum foil, made catalytically active as described previously, reduced further the oxygen concentration. A series of experiments was also conducted in which no special precautions were observed, other than to pre-electrolyze for periods of one to three hours, but the current was varied over

a much wider range (Table V). Experiments were made in electrolyte saturated with hydrogen and with nitrogen.

TABLE V

TYPICAL VALUES OF It_{max} WITH VARIATION OF CURRENT

Current, amp. $\times 10^6$	t_{max}, min.	It_{max}, microamp-min.	Dev'n. from It_{max} calculated, %
10.8	1.02	11.0	−11
6.03	2.04	12.3	− 1
2.57	4.74	12.2	− 2
1.59	7.25	11.5	− 7
1.11	10.7	11.9	− 4
0.777	16.7	13.0	+ 5
0.540	24.1	13.1	+ 6
0.443	27.2	12.1	− 3
0.214	59	12.6	+ 2

For a range of currents (0.21×10^{-6} to 10.8×10^{-6} amp.) t_{max} was observed to vary inversely with the current, I, such that the product It_{max} was constant (Table V).

Assuming the atoms in liquid mercury to be close-packed and the surface to be uniplanar, a value of 9.24Å^2 can be calculated from bulk density for the area occupied by a mercury atom at the liquid surface (14). From a knowledge of the effective area of a surface mercury atom and the true area of the cathode (4.3 cm.^{2}), and assuming the transference of one electron per surface mercury atom, a calculated value of 12.4 microamp-min. was obtained for the product It_{max}. The observed values of It_{max} were compared with the calculated value as shown in Tables II, III, IV, and V.

Of a total of 60 separate determinations of It_{max}, 46 were within 10% of the calculated value while the greatest deviation of a single experiment was 20%.

When small quantities of oxygen were introduced into pre-electrolyzed solutions, by the method previously described, It_{max} was markedly affected as shown by the solid line in Fig. 4. The dotted line represents the behavior

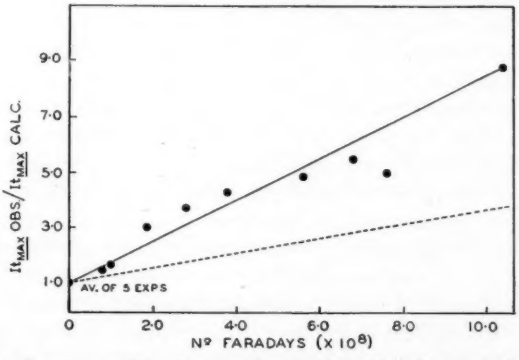

FIG. 4. Effect of oxygen on It_{max} (expressed as number of faradays passed to liberate oxygen in 1 liter of electrolyte).

that might be expected if all the oxygen in the system reacted with or was adsorbed on the electrode surface and was reduced with 100% current efficiency before any other process occurred. This would seem to support the view, previously stated, that chemisorbed oxygen is reduced with a very low current efficiency.

Mercury ion concentrations up to 2.0×10^{-7} mole per liter had no measurable effect on It_{max}.

After introducing mercury ions into the electrolyte by making the electrode anodic, the potential was allowed to reach a steady state on open circuit (curve I, Fig. 2*A*). The mercury surface was then renewed by overflowing the mercury cup, the potential was again allowed to reach a steady state (curve II, Fig. 2*A*), and the potential build-up curve was measured for the determination of t_{max}. Since the solubility product of mercury sulphide is about 10^{-53}, any sulphide ion (if present) would have been removed from the system when the cathode surface was renewed preceding the determination of curve II, Fig. 2*A*. It would seem unlikely, therefore, that some reaction involving sulphide or sulphide ion could account for the agreement between the calculated and measured values of It_{max}.

From the foregoing, it may be concluded that It_{max} corresponds to the amount of current necessary to transfer one electron across the electrode–solution interface for each mercury atom in the cathode surface. This one to one correspondence conceivably might be due to one of the following:

1. Oxygen present in the solution is adsorbed on, or in some manner reacts with, the mercury atoms of the cathode surface and is reduced when current is made to flow.

2. Some reducible impurity other than oxygen is adsorbed on the cathode surface and is reduced during the first few minutes of current flow.

3. A nonreducible impurity is adsorbed onto the mercury surface and the change of potential with current flow is the result of its desorption.

4. Hydrogen ions are discharged at the cathode where the resulting atoms are adsorbed by the surface mercury atoms in a one to one ratio. The point of maximum potential then corresponds to a complete monatomic film of hydrogen atoms on the mercury surface.

Quantitative studies on the influence of oxygen, reported in the literature, have been conducted through its effect on the Tafel line (cf. 4), a method that appears to be insensitive to oxygen concentrations lower than 10^{-5} molar (2). In the present work, the action of oxygen has been studied through its effect on the potential (Table I), potential decay curves (Fig. 2*D*), and the product It_{max} (Fig. 4). Of these three methods, potentials are the most sensitive to small amounts of oxygen at low concentrations. Introducing a quantity of oxygen into the system sufficient to react with only 2–3% of the cathode surface altered the electrode potential from -0.61 volt to about $+0.10$ volt. Such a marked effect would seem to indicate that when the potential remained at -0.61 volt for periods of one to two hours with or without stirring, the cathode surface could not have been contaminated with oxygen or oxide to a significant extent. Since the observed and calculated values of It_{max} were in

excellent agreement in the absence of significant quantities of oxygen (Table II), it would appear that the observed one to one correspondence cannot be explained on the basis of any reaction involving oxygen.

A reducible impurity other than oxygen, if it had been present in appreciable amount, presumably would also have markedly affected the value of It_{max}. The observed and calculated values of It_{max} were in good agreement (Table IV) for solutions that had not been pre-electrolyzed. Conversely, small quantities of such an impurity would surely have been reduced during the long periods of pre-electrolysis employed in many of the experiments (Table II). The one to one relation between the number of surface mercury atoms and the number of electrons equivalent to It_{max} cannot, therefore, be explained on the basis of any surface active reducible impurity that might possibly be present in the system.

The possibility that some nonreducible impurity might be responsible for the observed behavior seems rather remote. In this case, the change of potential with current flow would presumably correspond to the rate of desorption of the impurity, which in turn would be some function of an interfacial potential resulting from current flow. It does not seem possible to interpret the observed inverse relation between current and t_{max} (Table V) in terms of a current–potential relation. Moreover, if the change of potential from -0.61 volt to about -0.8 volt with current flow were due to the desorption of some material present in only "trace" amount, then a similar potential change in the opposite direction might be expected to take place when adsorption occurred after renewing the mercury surface. No such potential change was observed at any time.

Since the nature of this investigation makes it extremely difficult, if not impossible, to account for the observed results on the basis of impurities, it becomes necessary to consider the chemical components placed in the electrolyte by design. These are H^+, HSO_4^-, SO_4^{--}, water, and one of the gases hydrogen or nitrogen. For current to flow through an electrolytic cell, some chemical entity must be reduced at the cathode and another oxidized at the anode. The H^+ ion is the only substance likely to be reduced under the experimental conditions employed in this study. A reasonable explanation for the observed results would appear to be that when current is made to flow for the first time across a mercury surface, the H^+ ions reduced at the cathode are adsorbed as atomic hydrogen. This process is accompanied by a change of potential which is complete when each mercury atom at the surface accommodates one hydrogen atom. Secondary reactions involving current and responsible for potential changes probably occur as well, but if so, they do not appear to have a measurable effect on the value of It_{max} provided the initial potential build-up curves are established from zero potentials more negative than about $+0.15$ volt.

Potential change and rates of potential change attending that property of electrodes referred to as overvoltage have often been considered as resulting from the equivalent of a parallel mesh of resistance and capacitance at or near the electrode surface (cf. 10). Earlier work conducted in this labora-

tory (15), with copper and silver electrodes appeared to support this view. Two distinct types of potential build-up curves were observed, one of which (the initial curve) was believed to result from the deposition of a close-packed monatomic film of hydrogen on the electrode surface while the other was believed to result from the charging of a condenser.

The earlier view that, at t_{max}, the cathode accommodates a monatomic film of hydrogen would seem to receive support from the present study. However, since the film on mercury appears to be distributed in the ratio of one atom of hydrogen per surface atom of mercury, it now seems doubtful that similar film on a copper or silver electrode would be close-packed.

The electrode behavior of copper has been re-investigated since some of the conclusions drawn from the earlier work (15) appeared to be in doubt after the mercury cathode was investigated. Similar studies have been conducted with platinum electrodes. The results of these studies, which seem to support the conclusions drawn here, will be presented for publication in the near future.

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SILVER - SILVER ION EXCHANGE REACTIONS[1]

By A. Baerg and C. A. Winkler

ABSTRACT

The extent of the exchange between silver foils and silver ions in nitrate solution was compared with surface area measurements made by the Bowden-Rideal method. No quantitative correspondence between the two measurements was observed. During one hour the exchange with mechanically abraded surfaces affected about 30 apparent atomic layers of the metal, but this was reduced to about one-half this value when the surfaces were equilibrated for several days in inactive silver nitrate. Etched foils exchanged during one hour to a depth of only about 2 apparent atomic layers and this was not affected by equilibration. Bowden-Rideal area measurements gave values of roughly 7 and 15 times the planar area for etched and abraded specimens respectively. These values were not altered by equilibration of the surfaces. Only about 50% of the acquired radioactivity was subsequently removable in inactive silver nitrate solution. Part of the measured radioactivity was present on the surface in adsorbed ionic form and was not removable by a simple water wash. The magnitude of this adsorbed activity was found to be measurable electrometrically.

INTRODUCTION

It has been observed that the exchange between a metal and its ions in solution generally results in multiatomic layer exchange when based on the superficial area of the metal surface (8, 14, 4, 16, 13, 7). Since the effect of diffusion within solid metals is probably negligible, the deep exchange has usually been attributed to local cell action or other surface structural changes. While the effect of surface roughness has seldom been taken into account, some investigators have used exchange data for metals (5) or insoluble salts (11) as a direct measure of the true surface area. In the present study of silver surfaces prepared in several ways, the results of exchange experiments are compared with independent area measurements made by a modified Bowden-Rideal method (cf. (10)).

EXPERIMENTAL

Since this study was largely concerned with the effects of surface structure, the exchange reactions were restricted to silver solutions of one concentration: $3 \times 10^{-4}N$ in silver nitrate. The silver isotope, Ag^{110}, used as tracer was obtained from the National Research Council, Atomic Energy Project, Chalk River. This isotope is a beta and gamma ray emitter with a half-life of 270 days and was prepared by neutron irradiation of Nichols reagent grade silver nitrate in the nuclear reactor. The salt was dissolved in water to give a stock solution of active silver nitrate, the concentration of which was determined by titration of an aliquot against standard potassium iodide using eosin as indicator. Suitable quantities of active and inactive silver nitrate solutions were used to obtain the desired concentration and specific activity of the exchange solution.

Metallic silver disks, 2.5 cm.^{2} in apparent area and 0.004 in. in thickness,

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Contribution from the physical chemistry laboratory, McGill University, Montreal, Que., with financial assistance from the National Research Council of Canada.

were used in all the experiments. These were attached to holders so that both exchange and area measurements could be made with each specimen. A 24–40 standard taper re-entrant joint was fitted at each end with a lucite plug. The silver disk was cemented to the face of the plug at the re-entrant end by wetting the lucite with a drop of chloroform. A silver spring pressed against the back of the disk, through a hole in the center of the plug, to establish electrical contact with a brass rod through the middle of the joint.

The exchange cell was a 500 ml. round bottom flask with 24–40 standard taper inlets to accommodate the electrodes. A close-fitting constant speed stirrer was used to agitate the exchange solution which was maintained oxygen-free by a stream of nitrogen purified over hot copper. The 400 ml. of solution in this cell contained about 0.3 mc. of radioactive silver and sufficient total silver ion to preclude significant alteration of the ratio of active to inactive silver during any one experiment.

The radioactivity acquired by the silver during exchange was determined with standard counting equipment using an end-window Geiger tube. The lead castle was suitably fitted with a tapered holder to position the electrode about 5 cm. from the tube window. All electrodes used gave the same counting rate, within statistical fluctuations, for equal amounts of radioactive silver. Corrections for background and a small amount of activity adsorbed on the glass were made by counting after the active silver foil was removed from the electrode assembly. These corrections were both less than 100 counts per minute while the activity on the silver was usually greater than 1000 counts per minute. Corrections for decay of the radioactive silver were automatically made by use of an active electrode as a counting standard. It was calibrated by electrodeposition of a known amount of active silver from a silver nitrate electrolyte. For calculation of the apparent depth of exchange, the amount of silver exposed on 2.5 cm.^{2} true surface was taken as 6.2×10^{-9} gm-atom.

The apparatus and experimental procedures for the Bowden-Rideal area measurements were similar in all essential respects to those used previously in this laboratory (10, 15, 19).

RESULTS

Preliminary experiments were made with silver foils prepared by abrasion with a water slurry of emery on glass. These surfaces gave Bowden-Rideal areas which depended strongly on the pressure applied during abrasion. The exchange affected hundreds of apparent atomic layers of the metal and continued indefinitely, though slowly. Thus, a specimen which measured 52 times the planar area exchanged to a depth of 330 atomic layers during 13 days. However, only a small fraction of the acquired activity was subsequently removable in inactive silver nitrate solution. This appeared to indicate that local cell action played a predominant role in the exchange process.

In an attempt to separate the influence of local cell processes from a reversible exchange the effect of preliminary equilibration in inactive solution was examined. The cell used for equilibrating the specimens was similar to the exchange cell and both solutions were $3 \times 10^{-4}N$ in silver nitrate. Speci-

mens prepared by abrasion with emery and surfaces etched with 7*N* nitric acid were studied. For comparison, a one hour period of exchange was selected while the time of equilibration was varied. Following the exchange, the electrodes were thoroughly rinsed with water and Bowden-Rideal areas determined. The surfaces were then dried and the acquired radioactivity measured. The results of these experiments are summarized in Table I.

TABLE I

DEPENDENCE OF EXCHANGE ON SURFACE PREPARATION. EXCHANGE TIME—ONE HOUR

Electrode	Equilibration time, hr.	Apparent atomic layers exchanged	Bowden-Rideal area (times planar)
Emery surfaced foils			
1	0	36.8	15.2
2	0	24.5	14.5
3	10	13.2	14
4	35	20.5	17.6
5	75	21.2	18
6	80	19.2	19
7	288	12.6	21.5
8	360	14.5	14.7
9	360	13.5	13.5
10	408	13.7	14.8
11	408	15.5	16.0
Etched foils			
1	0.3	2.0	6.4
2	3.5	3.4	10.0
3	6.5	3.0	9.5
4	14	2.0	8.0
5	22	2.6	7.3
6	25	1.9	7.4
7	25	2.2	7.2
8	36	2.7	7.5
9	40	2.7	7.9
10	48	2.5	9.7
11	53	2.5	11.0

Although the metal surfaces were poorly reproducible in respect of both exchange and area, some general trends became apparent. Equilibration of abraded surfaces for several days reduced the exchange from about 30 to 15 atomic layers but had no apparent influence on the Bowden-Rideal areas, which were roughly 15 times planar. Similarly, the areas of etched surfaces were not affected and their magnitude was only about one-half that for abraded specimens. On the other hand, the exchange with these surfaces showed a maximum value, during one hour, of only 3.4 atomic layers and this also appeared to be unaffected by equilibration. These results indicate that for abraded foils the local cell action is diminished and the reproducibility of the surfaces in respect of exchange appears much improved by equilibration (cf. emery surfaced electrodes 1 and 2, Table I). However, the local action was evidently not eliminated for either the etched or abraded

specimens since only 50% to 60% of the acquired activity was subsequently removable by exchange with inactive solution.

The observed exchange appeared from the above experiments to be due in large measure to local surface reactions. Some additional experiments with etched foils, however, suggested that about 25% of the measured activity was present on the surface in ionic form and was not removed by the water wash following the exchange. When an already radioactive etched electrode was again rendered cathodic in the overvoltage cell of the Bowden-Rideal apparatus and then immediately rinsed with water and reimmersed in active solution, it acquired additional radioactivity equivalent to 0.5 to 1 atomic layer of the metal. By repetition of the operations addition of activity could be continued indefinitely. Presumably, adsorbed active silver ions not removed by the water wash were subsequently electrodeposited when the metal was rendered cathodic in the overvoltage cell.

To examine this view further, experiments were made to observe the possible influence of adsorbed silver ions on the overvoltage–time curves obtained with the Bowden-Rideal apparatus. In Fig. 1 is shown the manner in which the

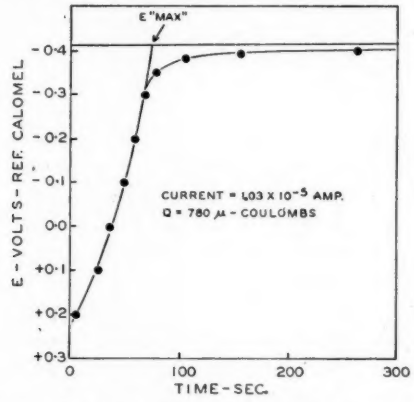

FIG. 1. Change of potential with time at a silver cathode during electrolysis in $N/5$ sulphuric acid.

silver cathode potential varies with time (at constant current) during electrolysis, just after immersion in the $N/5$ sulphuric acid electrolyte. It seemed reasonable that in the initial presence of adsorbed silver ions their quantity should be related to the amount of electricity, Q, consumed in the attainment of the hydrogen overvoltage (E_{max}). Campbell and Thomas (3) have made use of such curves to determine the thickness of oxide films on metals. In the present experiments the value of Q was obtained by extrapolation of the steep part of the curve to "E_{max}" as indicated. The value of the time, t, at the point of intersection, multiplied by the constant current was taken to give Q.

In a series of experiments made with an etched electrode, the activity gained from the radioactive solution, following cathodic treatment in the overvoltage cell, was compared with the Q values determined immediately

after removal from the active solution. The freshly etched specimen was first rendered cathodic in the overvoltage cell, then rinsed with water and transferred to the active exchange solution for one minute. Following this it was again rinsed and Q determined as described above. After the acquired radioactivity was measured, the electrode was again rendered cathodic in preparation for the second experiment. The whole process was repeated five times with this electrode; the results are recorded in Table II. The total activity

TABLE II

EFFECT OF CATHODIC TREATMENT. ETCHED SILVER ELECTRODE

Electrode	Exchange time, min.	Total activity	Q	Activity gain
		Microcoulombs		
1	1	1960	580	1960
2	1.5	2580	530	620
3	1	3080	530	500
4	1	3540	535	460
5	1	4140	560	600
6	1	4830	590	690

Mean activity for 2, 3, 4, 5, and 6 = 570 microcoulombs
Mean value of Q for 2, 3, 4, 5, and 6 = 550 microcoulombs

and the increase in activity in each experiment are expressed as coulombic equivalents for comparison with Q. These data reveal that the activity gained in each experiment following the first is in good agreement with the corresponding value of Q. Similar results were obtained in another series for which the immersion time in active solution was increased to 5 to 10 minutes. Presumably the activity acquired by the metal in the first experiment was due largely to an exchange process while in subsequent experiments the activity gain was due to an adsorption effect.

In addition to these results the value of Q was found to be linearly related to the logarithm of the silver ion concentration in the solution from which adsorption had taken place. The data represented in Fig. 2 were obtained using inactive silver sulphate solutions to avoid the possibility of side effects in the overvoltage cell (containing $N/5$ sulphuric acid) due to the nitrate ion. Concentrations of 10^{-2}, 10^{-4}, 10^{-6}, and 10^{-8} equivalents per liter in silver ion were used and the solutions were maintained oxygen free by bubbling pure nitrogen through them.

From the slope of the semilogarithmic plot of the data it is possible to calculate an adsorption capacity, C, as

$$C = \Delta Q \Big/ \frac{2.3\ RT}{nF}\ \Delta \log\ [Ag^+].$$

The values thus obtained, in μf. per cm.^{2} (apparent area of electrode = 2.5 cm.^{2}), for three different electrodes, together with the capacities obtained

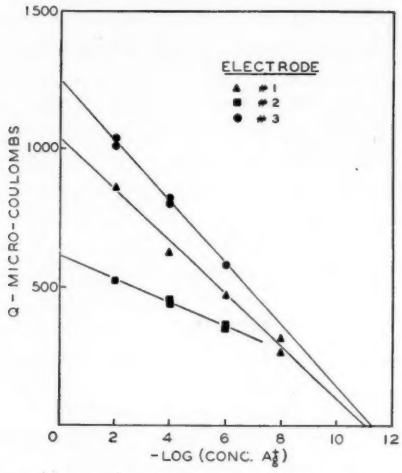

FIG. 2. Relation between Q and logarithm of silver ion concentration.

by the Bowden-Rideal measurements after adequate electrolysis (19), were as follows:

Electrode	1	2	3
Bowden-Rideal capacity (μf.)	150	145	165
Adsorption capacity (μf.)	610	250	745

While the Bowden-Rideal values were all about 150 μf. per cm.^{2}, the adsorption capacities were two to five times greater. It is at present difficult to account for this discrepancy. These experiments however showed that the Q values gave a reasonable measure of the adsorbed activity.

Hevesy and Blitz (9) have suggested that the presence of an adsorbed ionic double layer reduced the rate of exchange between lead ions and radioactive lead sol. Several series of experiments with etched silver electrodes appeared to indicate a similar behavior. The electrodes of one group were equilibrated for 15 hr. in inactive silver nitrate solution and therefore retained an adsorbed layer of inactive ions before commencement of the exchange reaction. Several electrodes in a second group were rendered cathodic in the overvoltage cell just prior to exchange, and were therefore free of adsorbed ionic silver. The time of exchange was varied among the different specimens to obtain a picture of the kinetic behavior for the two groups of electrodes. Though the surfaces were poorly reproducible, it was evident that several hours were required for the equilibrated electrodes to gain roughly the same total activity (about 3 apparent atomic layers) as that acquired by nonequilibrated surfaces in a rapid initial exchange of only several minutes duration. The adsorbed activity was roughly the same for all electrodes so that the more rapid gain of activity by the fresh specimens must have been due to a more rapid atom–ion exchange.

DISCUSSION

Although the extent of exchange during one hour with well-equilibrated

surfaces of abraded silver was in reasonable agreement with the Bowden-Rideal area, wide deviations occurred with all other specimens. This seems to imply that either the exchange or the Bowden-Rideal capacity or both are not directly dependent on the actual area of the metal surface. The method which has been found suitable for determination of the adsorbed silver ions implies that the potential change in the initial attainment of the hydrogen overvoltage is due to metal ion polarization. There remains the question of whether the linear potential buildup of the Bowden-Rideal capacity measurement, following adequate electrolysis and discharge of potential, involves a similar electrode process. If it does, it would seem doubtful that such a capacity measurement is dependent on the true surface area.

Variations in exchange behavior may reasonably be attributed to differences in the submicroscopic structure of the crystalline metal surfaces. The theories of crystal growth, as laid down by Volmer (18) and by Kossel and Stranski (17) predict marked differences in the binding energy of atoms on a crystal surface, depending on the number of atoms surrounding the one in question. An average crystal surface in equilibrium with its solution is visualized as consisting of a series of steps or incompleted atomic layers. The edges of these steps will be straight at the absolute zero of temperature but at higher temperatures they will present a kinked appearance. In addition there will be a number of atoms *on* the terraces between steps with a corresponding number of lattice vacancies in the surfaces. The out-of-lattice atoms are probably highly mobile (1) and may be regarded as a "2-dimensional gas phase" in equilibrium with the atoms at step positions. On the basis of nearest neighbor interactions, these are readily seen to be more strongly bound than those on the surface. Accordingly exchange between ions in solution and crystal surface atoms may be considered to occur most easily by a two way process: (1) exchange of ions with relatively few out-of-lattice atoms on the terraces and (2) interchange of position of the latter with atoms at step positions. This interchange will be facilitated by the existence of kinks in the steps and statistical fluctuations of these will result in incorporation of radioactive atoms into the surface layers. Consideration of the energy required to remove an atom from within a flat surface essentially excludes the possibility of significant exchange by such a direct process. Paneth (12) and Zimens (20) have made use of these concepts to explain the differences in exchange behavior of well-formed natural crystals in contrast to that of precipitated crystals of insoluble salts.

Burton and Cabrera (2) have made an investigation of the concentration of steps or "Frenkel terraces" on a crystal surface in equilibrium. Surfaces are divided into classes, close-packed and stepped. A close-packed crystal face is defined as one in which all the surface atoms are at the same distance from a plane parallel to the face. In all other cases the surface will present a stepped appearance. By way of illustration, in the simple cubic system, (100) and (110) faces are close-packed and all others stepped. In a stepped surface, the terraces are pieces of close-packed surface. For faces of high index the terraces will be (100) surfaces. Calculations also show that the concentration of lattice

vacancies in a close-packed surface in equilibrium is very small, while the concentration of kinks in a step in equilibrium is high.

It is now easy to understand the different results obtained in the present exchange experiments. Mechanical abrasion may be expected to cleave the silver crystallites on the surface in a variety of directions, to expose a virtually infinite number of crystal faces with completely random orientations (of both low and high indices). Aside from increasing the over-all exposed area this is precisely the condition which should lead to the extensive exchange observed, by way of steps on faces of high index.

On the other hand, with etched foils which showed relatively little exchange, the etching process should, according to the theories, occur largely at the edges of incompleted atomic layers. The steps, largely responsible for exchange, will then tend to disappear leaving the crystallites surrounded by a relative preponderance of low index (nonexchanging) surfaces.

Superimposed on the exchange with surface atoms on crystal faces is the deep seated exchange that presumably results from local cell action. It is well known that different crystal faces exhibit dissimilar chemical reactivities. These differences may be attributed to differential bonding along the few principle directions within the crystal lattice (17). Fricke (6) has calculated the work of formation of crystal surfaces for various metals. For silver he has found 1934 and 1643 erg per cm.^{2} per atom for the (001) and (111) crystal faces respectively. For crystals in contact with solution these energy differences may be expected to produce slow "anodic" dissolution of incomplete atomic layers on those faces consisting of terraces of low binding energy with corresponding growth of the terraces of higher binding energy (cathodic regions). As the process continues the steps on the surfaces will tend to disappear, hence the number of exchangeable atoms (at step positions) decrease. This would seem to account for the reduced exchange observed with equilibrated specimens of abraded silver foils.

Although the above interpretation of the exchange results seem reasonable, it is probably oversimplified. Adsorbed solvent or ionic material probably would alter the exchange processes quite markedly. A detailed kinetic study of the reaction on individual surfaces would be desirable.

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THE USE OF INFRARED SPECTROPHOTOMETRY FOR THE ESTIMATION OF SMALL QUANTITIES OF SOME HALOGENATED HYDROCARBONS[1]

By L. Breitman[2] and E. W. R. Steacie

ABSTRACT

The infrared spectra of chloral, carbon tetrachloride, and chloroform have been determined between 1500 and 650 cm.$^{-1}$ over a range of pressures in the gas phase. Absorption bands suitable for the quantitative analysis of binary and ternary mixtures of the components have been selected and their peak intensities shown to obey Beer's Law over the range of pressures studied. Ternary mixtures have been analyzed from the spectra with an accuracy of about 20%.

The spectra of dichloromethane and methyl chloride have also been measured under comparable conditions.

INTRODUCTION

Kinetic studies of the decomposition of many organic compounds have been made possible by the perfection of techniques used in estimating the small quantities of hydrocarbons that are produced when the decomposition is studied at low conversions. Investigations of the degradation of chlorine-containing compounds have been somewhat handicapped by the difficulties encountered in the analysis of halogenated hydrocarbons in a large excess of the parent substance.

The present problem arose in connection with the photolysis of chloral. This reaction, if analogous to that of acetaldehyde, proceeds by: (1) an intermolecular rearrangement and/or (2) rupture of the C–C bond:

$$CCl_3CHO + h\nu \rightarrow CHCl_3 + CO \qquad (1)$$

$$CCl_3CHO + h\nu \rightarrow CCl_3 + CHO \qquad (2)$$

followed by the abstraction reactions

$$CCl_3 + CCl_3CHO \rightarrow CHCl_3 + CCl_3CO$$

$$CCl_3 + CCl_3CHO \rightarrow CCl_4 + CCl_2CHO$$

Carbon monoxide was found to be the only 'noncondensable' product in a preliminary photolysis of chloral, but presumably because of insufficient differences in the vapor pressures of the condensable products, no other pure components could be isolated by distillation from a Ward still. It seemed reasonable to assume that the mixture resulting from the photolysis of chloral contained chloroform and carbon tetrachloride in a large excess of the aldehyde.

This paper describes a method of detecting and estimating the components of a mixture of chloral, carbon tetrachloride, and chloroform with the infrared spectrophotometer.

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EXPERIMENTAL

Apparatus

The optical cell was of pyrex, 10 cm. long, to which plane polished sodium chloride windows were affixed with Benolite cement. The cylindrical cell, of total volume 139.3 cc., was provided with a stopcock and ground glass joint to permit filling and evacuation, and a cold finger for condensation of gas samples.

The gas samples to be analyzed were prepared in a suitable high vacuum line containing liquid air traps, calibrated volumes, and a high speed, two-stage mercury diffusion pump. Dow Corning high vacuum silicone grease was used on all joints and stopcocks to minimize absorption of the samples. The optical densities of the gases were measured with a Perkin-Elmer Model 21 double beam recording infrared spectrophotometer (1, 4, 5) using a sodium chloride prism.

Materials

Chloral was a Fisher Scientific Company product of unspecified purity. It was distilled in air at a 5:1 reflux ratio. The portion boiling constantly at 97.8° C. was distilled *in vacuo* through a U-tube containing anhydrous phosphorus pentoxide and stored in a dark brown bottle. This product had a vapor pressure of 49.5 mm. at 24.4° C. and melted at −59° C.

Carbon tetrachloride, reagent grade, was obtained from Merck and dichloromethane, research grade, from Anachemia. Both compounds were distilled *in vacuo* and stored in the dark.

Chloroform was a Mallinckrodt analytical reagent grade product. It was passed through a column of silica gel before use to remove traces of alcohol and water.

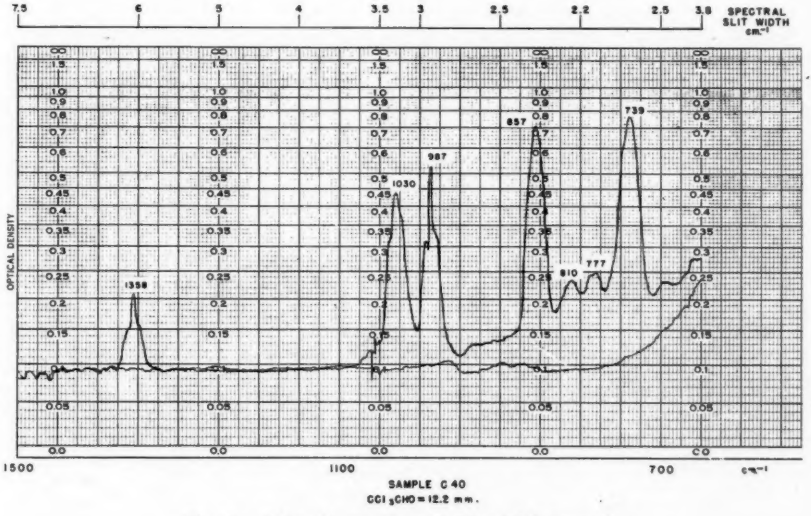

FIG. 1. Infrared spectrum of chloral (12.2 mm.).

Methyl chloride of unspecified purity was obtained from the Matheson Company and was purified by repeated bulb-to-bulb distillations *in vacuo*.

RESULTS AND DISCUSSION

Spectra of the Individual Components

Typical infrared spectra of chloral, carbon tetrachloride, and chloroform

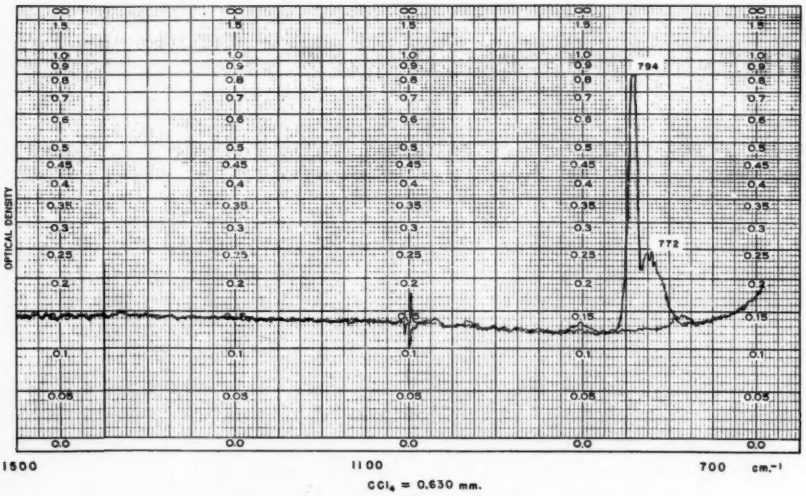

FIG. 2. Infrared spectrum of carbon tetrachloride (0.630 mm.).

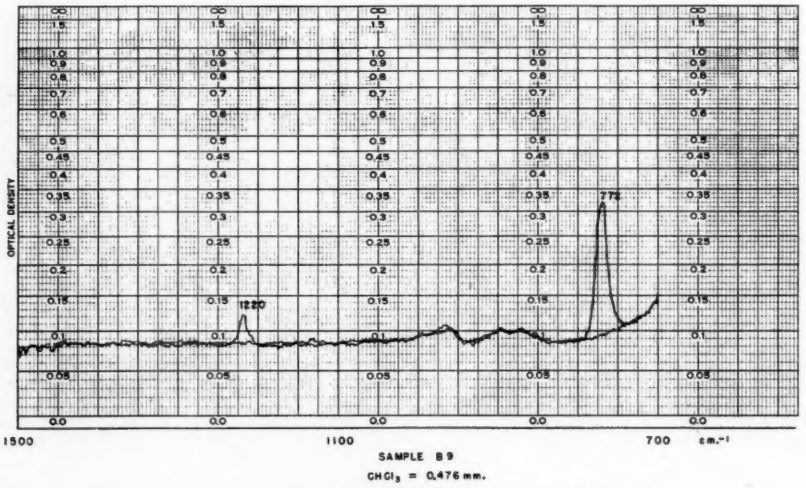

FIG. 3. Infrared spectrum of chloroform (0.476 mm.).

are reproduced in Figs. 1–3 respectively. All measurements were made at comparable spectral slit widths without a matching optical cell in the control beam of the spectrophotometer. The lower lines in Figs. 1–3 were obtained with the optical cell evacuated and all optical densities were measured from these reference lines. Inspection of these spectra suggested that the strong band of carbon tetrachloride at 794 cm.$^{-1}$ and the weaker, but distinctive band of chloroform at 1220 cm.$^{-1}$ might serve most conveniently for the analysis of these two components. The stronger chloroform band at 772 cm.$^{-1}$ is less suitable because of overlap with both carbon tetrachloride and chloral absorp-

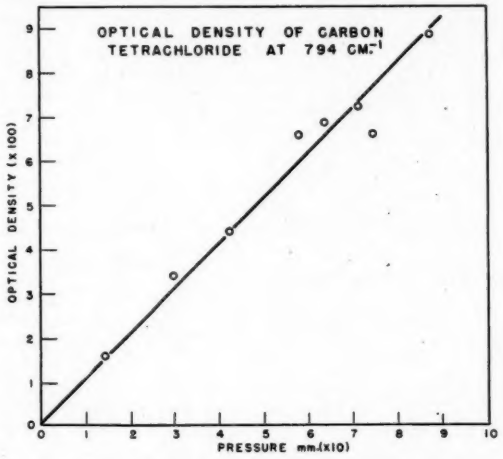

FIG. 4. Optical density of carbon tetrachloride at 794 cm.$^{-1}$

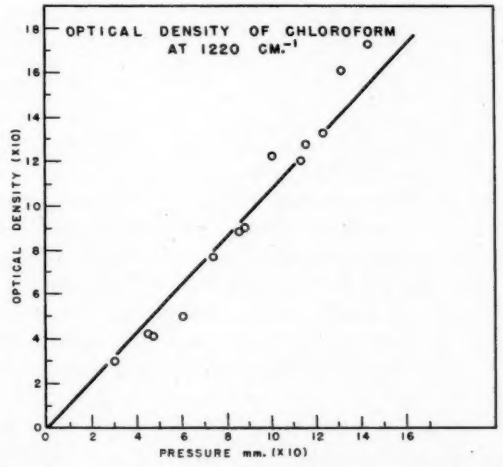

FIG. 5. Optical density of chloroform at 1220 cm.$^{-1}$ as a function of pressure.

tion. The conformity of these bands with Beer's Law is shown by the linear plots of peak optical density against partial pressure in Figs. 4 and 5. The numerical data are given in Tables I and II.

TABLE I

OPTICAL DENSITY OF CARBON TETRACHLORIDE

Sample	Pressure, mm.	Optical density	
		794 cm.$^{-1}$	772 cm.$^{-1}$
A8	0.421	0.440	0.076
A9	0.292	0.338	0.056
A10	0.120	0.156	0.026
A11	0.633	0.686	0.120
A12	0.742	0.685	0.133
A13	0.710	0.720	0.133
A14	0.869	0.885	0.180
A16	0.568	0.656	0.116

TABLE II

OPTICAL DENSITY OF CHLOROFORM

Sample	Pressure, mm.	Optical density	
		769 cm.$^{-1}$	1220 cm.$^{-1}$
B1	0.574	0.266	.....
B2	1.41	0.695	.....
B3	1.16	0.660	0.127
B4	0.859	0.450	0.088
B5	1.32	0.726	0.160
B6	1.44	0.800	0.172
B7	0.888	0.467	0.090
B8	1.01	0.601	0.122
B9	0.476	0.225	0.041
B10	0.746	0.392	0.077
B11	1.14	0.582	0.120
B12	0.457	0.213	0.042
B13	1.24	0.610	0.132
B14	0.304	0.142	0.030
B15	0.610	0.285	0.050

Chloral in the liquid phase exists in equilibrium with its trimer. The latter can be removed by simple distillation, but the equilibrium concentration of the trimer, about 10% (3), is attained on standing. The presence of the trimer in the gas phase, however, was not detected: there were no significant differences between the infrared spectrum of stored chloral and that of the freshly distilled material. The aldehyde absorbs moisture to precipitate the hydrate and decomposes readily on exposure to light or oxygen in the atmosphere (2). To obtain reproducible spectra it was necessary to dry the chloral quite frequently by passage over phosphorus pentoxide and to store it in the dark after distillation.

The infrared spectrum of chloral has major peaks at 1358, 1030, 987, 857, and 739 cm., and two small maxima at 777 and 810 cm.$^{-1}$. The relative magnitudes of absorption at 857, 739, 777, and 810 cm.$^{-1}$ were useful criteria for

purity of the aldehyde. Pure chloral is practically transparent at 1250–1200 cm.$^{-1}$. The appearance of appreciable structure in this region probably denotes decomposition of the compound. This phenomenon is of importance because of overlap with the peak at 1220 cm.$^{-1}$ in the spectrum of chloroform. The optical densities of chloral at 794 cm.$^{-1}$ and 772 cm.$^{-1}$ were also measured because the spectrum of carbon tetrachloride shows maxima at these positions and there are no peaks in the carbon tetrachloride spectrum where chloral is transparent. The data for the optical densities of chloral at the important

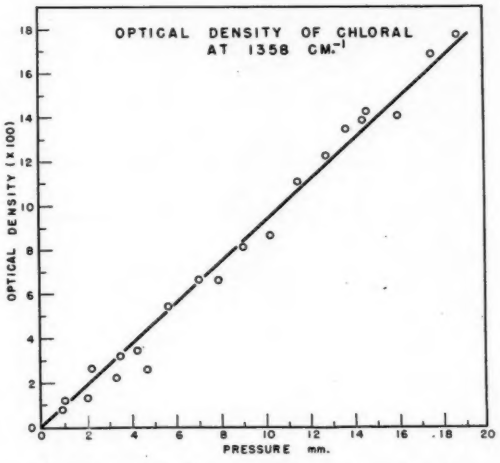

FIG. 6. Optical density of chloral at 1358 cm.$^{-1}$ as a function of pressure.

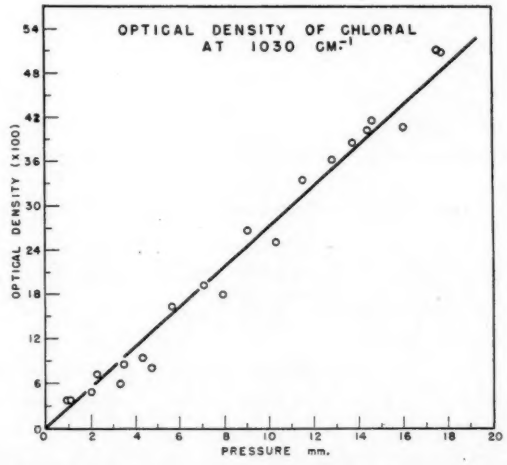

FIG. 7. Optical density of chloral at 1030 cm.$^{-1}$ as a function of pressure.

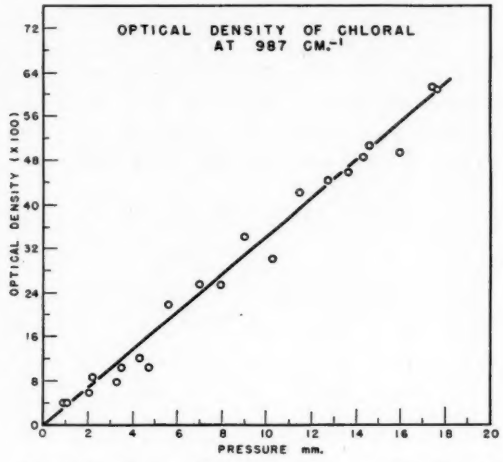

FIG. 8. Optical density of chloral at 987 cm.$^{-1}$ as a function of pressure.

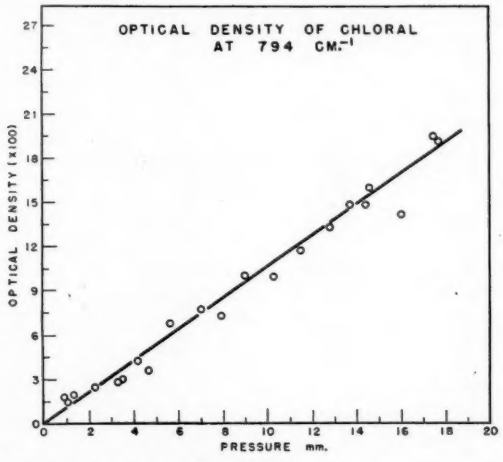

FIG. 9. Optical density of chloral at 794 cm.$^{-1}$ as a function of pressure.

wave numbers are collected in Table III, and the conformity with Beer's Law established by the linear plots in Figs. 6–9.

Spectra of Mixtures

Table IV lists the analytical results obtained for a series of mixtures of chloral, carbon tetrachloride, and chloroform. The infrared spectrum of a typical mixture is reproduced in Fig. 10.

Chloroform and carbon tetrachloride are transparent at 1358, 1030, 987, and 857 cm.$^{-1}$ where chloral has spectral peaks. The optical densities at these

TABLE III

OPTICAL DENSITY OF CHLORAL

Sample	Pressure, mm.	Optical density, cm.$^{-1}$						
		1358	1030	987	857	794	772	739
1C	10.24	0.086	0.251	0.300	0.523	0.097	0.106	0.512
3C	13.70	0.134	0.383	0.455	0.650	0.147	0.153	0.652
4C	14.60	0.142	0.412	0.505	0.714	0.158	0.160	0.713
5C	17.50	0.168	0.508	0.610	0.816	0.194	0.212	0.810
13C	5.59	0.054	0.162	0.216	0.342	0.067	0.094	0.338
14C	7.91	0.066	0.176	0.252	0.382	0.073	0.105	0.386
15C	4.68	0.026	0.080	0.104	0.162	0.035	0.047	0.162
16C	3.47	0.032	0.083	0.104	0.166	0.030	0.036	0.166
17C	3.29	0.022	0.060	0.078	0.126	0.028	0.035	0.133
18C	2.00	0.013	0.048	0.058	0.085	0.020	0.023	0.096
19C	0.911	0.008	0.038	0.043	0.061	0.018	0.022	0.070
30C	7.00	0.066	0.192	0.254	0.364	0.076	0.074	0.394
31C	16.00	0.140	0.404	0.490	0.718	0.140	0.143	0.702
32C	14.40	0.138	0.398	0.482	0.712	0.146	0.140	0.702
33C	11.45	0.110	0.332	0.418	0.614	0.116	0.116	0.623
34C	12.80	0.122	0.360	0.440	0.676	0.132	0.128	0.668
35C	17.70	0.170	0.508	0.605	0.858	0.190	0.198	0.860
36C	1.02	0.012	0.036	0.043	0.060	0.015	0.014	0.074
37C	9.00	0.081	0.266	0.340	0.510	0.099	0.094	0.522
38C	4.28	0.034	0.094	0.120	0.194	0.039	0.035	0.196
39C	2.20	0.026	0.074	0.087	0.143	0.025	0.025	0.145

TABLE IV

ANALYSIS OF SYNTHETIC MIXTURES

Sample	Composition of mixture, mm.		Infrared analysis,* mm.	
M1	CCl_3CHO:	8.52	CCl_3CHO:	9.9
	CCl_4:	0.312	CCl_4:	0.27
M2	CCl_3CHO:	18.9	CCl_3CHO:	19.9
	CCl_4:	0.328	CCl_4:	0.30
M3	CCl_3CHO:	10.1	CCl_3CHO:	10.8
	$CHCl_3$:	0.610	$CHCl_3$:	0.55
M4	CCl_3CHO:	4.61	CCl_3CHO:	4.3
	$CHCl_3$:	0.821	$CHCl_3$:	0.65
M6	$CHCl_3$:	0.719	$CHCl_3$:	0.78
	CCl_4:	0.802	CCl_4:	0.70
M7	$CHCl_3$:	0.558	$CHCl_3$:	0.50
	CCl_4:	0.630	CCl_4:	0.44
M8	CCl_3CHO:	5.56	CCl_3CHO:	5.0
	CCl_4:	0.480	CCl_4:	0.57
	$CHCl_3$:	0.462	$CHCl_3$:	0.49
M9	CCl_3CHO:	5.13	CCl_3CHO:	4.8
	CCl_4:	0.470	CCl_4:	0.40
	$CHCl_3$:	0.330	$CHCl_3$:	0.31

* *The data for chloral in this column are average values from optical density measurements at appropriate wave numbers.*

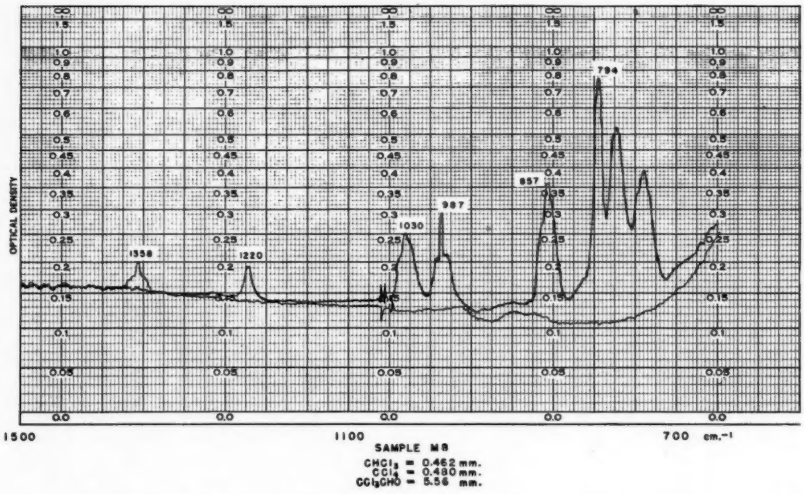

FIG. 10. Infrared spectrum of a typical mixture of chloroform, carbon tetrachloride, and chloral.

wave numbers, obtained from the infrared spectrum of a mixture of chloral, carbon tetrachloride, and chloroform, then give directly the concentration of chloral in the mixture. The chloroform content is measured similarly from the optical density at 1220 cm.$^{-1}$ since the spectra of both carbon tetrachloride and chloral show no structure at this wave number.

Since chloroform is practically transparent at 794 cm.$^{-1}$, the optical density of the mixture at this wave number, less the contribution of the previously determined quantity of chloral, is used to estimate the concentration of carbon tetrachloride.

A sample calculation is given for the analysis of sample M8:

Optical density at 1358 cm.$^{-1}$ = 0.054, equivalent to 5.5 mm. chloral
" " " 1030 cm.$^{-1}$ = 0.128, " " 4.7 mm. "
" " " 987 cm.$^{-1}$ = 0.166, " " 5.0 mm. "
" " " 857 cm.$^{-1}$ = 0.247, " " 4.9 mm. "

Mean value of concentration of chloral = 5.0 mm.

Optical density at 1220 cm.$^{-1}$ = 0.054, equivalent to 0.49 mm. chloroform
Optical density at 794 cm.$^{-1}$ = 0.650
Optical density at 794 cm.$^{-1}$ due to 5.0 mm. of chloral = 0.054
" " " " " " 0.49 mm. " chloroform = 0.000
" " " " " " carbon tetrachloride
= 0.650 − 0.054
= 0.596, equivalent to 0.57 mm. of carbon tetrachloride.

The deviations between the data for the synthetic mixtures and those obtained spectrophotometrically in Table IV are due mainly to the difficulty

in preparing mixtures whose composition in the gas phase is accurately known. The chlorinated compounds dissolve to some extent in the Silicone grease used in the vacuum line and the Benolite cementing the sodium chloride windows to the pyrex optical cell. The extent of absorption is a function of the time of exposure of the compounds to grease, the surface area of the grease, and the pressure at which the gaseous sample is prepared. Under these circumstances, it is not feasible to make empirical corrections for the absorption effects.

A standard procedure in preparing and analyzing the samples was adhered to as closely as possible. While reproducible data were obtained in this way, it is felt that the elimination of stopcocks wherever possible would considerably increase the accuracy of analysis of these chlorinated compounds by infrared spectrophotometry.

Spectra of Other Chlorinated Hydrocarbons

With a view to extending these studies to more complex mixtures of chlorinated hydrocarbons, the infrared spectra of dichloromethane and methyl chloride have also been measured at 1 mm. and 10 mm. respectively under comparable experimental conditions.

The absorption bands in these compounds are relatively weak; dichloromethane showed maxima at 1277, 1262, 762, and 747 cm.$^{-1}$ and methyl chloride at 1370, 1340, 745, 726, and 710 cm.$^{-1}$

ACKNOWLEDGMENTS

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PHYSICOCHEMICAL EFFECTS OF RADIO-FREQUENCY FIELDS[1]

By H. H. Yates[2] and C. A. Winkler

ABSTRACT

The outgassing of liquids has been studied under a variety of conditions including the application of a radio-frequency electric field. A large acceleration of the outgassing rate in the electric field was shown to result from convection currents established by the temperature gradient set up by the field. The significance of such a temperature gradient in a comparison of the chemical behavior in such a field with that under normal thermal conditions has been considered. When account was taken of the thermal gradients induced by the field, a field of approximately 2000 volts per cm. and 1.5 megacycles had no measurable effect on the rate of polymerization of styrene in bulk at 80°C.

INTRODUCTION

In a previous paper from this laboratory (2) it was reported that the bulk polymerization of styrene was inhibited by as much as 80% in the presence of a radio-frequency electric field. In these experiments, as in commercial practice, temperature was measured with an alcohol thermometer, and it was believed that the observed inhibition could not be attributed to thermal effects. It was later found (9) that both alcohol and mercury thermometers, suspended in the vapors of a boiling liquid, have higher than normal readings in the electric fields used. A method was therefore devised by which a thermocouple–potentiometer arrangement was used to compare the temperature of a field reaction with that of a control reaction. Under conditions similar to those used in the polymerization study, the decomposition of benzoyl peroxide in toluene solution was apparently inhibited, although analytical difficulties at the low concentrations used seemed to be a source of considerable error. A red color appeared about an hour earlier in the field reaction than in the control reaction. When nitrogen was bubbled through the system, neither the control nor the field reaction suffered this color change.

These results were sufficiently interesting to encourage further study of a similar reaction, and the decomposition of benzene diazoacetate, described in detail by Waters and others (1, 3, 7, 12), was finally chosen for the purpose. The kinetics of this reaction may be studied over a wide range of concentrations by measuring the evolution of nitrogen. This eliminates the necessity for sampling the reaction mixture, with attendant readjustments to the electrical system.

EXPERIMENTAL AND RESULTS

In preliminary experiments, both a control cell and a field cell were used, and the reactions were followed by measuring the increase in nitrogen pressure at constant volume in a partially evacuated system. At high concentrations, where the pressure increase was derived mainly from the decomposition of benzene diazoacetate, the effect of the field was negligible. However, at very low concen-

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trations, where the pressure increase was due largely to the release of dissolved gas into the partial vacuum, the field caused a marked acceleration. Subsequent experiments established that the field caused a large increase in the rate of the outgassing process, which increased with the dielectric constant of the liquid, but was not significantly different for different gases. Improved reproducibility was necessary for a detailed study of the effect. In the method finally adopted a single cell was used, and the field was applied for only a part of each experiment. Nitrogen dissolved in methyl benzoate was the only system studied in detail by this more precise method.

The equipment for applying the radio-frequency field has been described by Bryce *et al.* (2). There was also a cell to hold the gas–liquid solution and a pressure measuring system. The cell was a pyrex cylindrical annulus about 10 cm. high, 6 cm. in outside diameter, and 1 cm. thick. It incorporated two outlets and a well. One outlet, fitted with a ground glass ball joint, was connected through a flexible spiral of 3 mm. tubing to the pressure measuring system. The other outlet, with a 10/30 standard taper joint, was used for a variety of purposes, including flushing, filling, saturating, and stirring. The well served to hold the thermocouple used for temperature determinations. Copper electrodes, fixed externally to the cell walls with liquid solder, formed a capacitor in which the dielectric was composed of the pyrex cell walls and the solution.

Pressures were measured on a mercury manometer connected directly to the cell. The mercury level in the pressure arm was maintained constant with a levelling bulb during an experiment. Partial evacuation of the system was accomplished by connecting it momentarily to an evacuated bulb of suitable size.

The cell was immersed in a constant temperature bath to within half an inch of the top of the outlets. Adequate flow of oil around the electrodes was ensured by a propeller attached to the end of a glass shaft extending down through the "core" of the cell. The temperature was determined by the thermocouple method (9). A potentiometer was maintained in balance with a thermocouple placed in an auxiliary thermostat at the desired temperature. A thermocouple was held near the same temperature by storing it in a well in the thermostat containing the cell. To determine the temperature of the solution, the second thermocouple was transferred to the cell just as the field was turned off. The potentiometer was immediately switched to record the temperature of this thermocouple, which was found to rise to the cell temperature in about three seconds, remain steady for about five to eight seconds, and then begin to fall as the heat supplied by the field was dissipated.

The cell was carefully cleaned and dried before each experiment. The quantity of solution used was just sufficient to cover the electrodes (about 90 ml.). The pressure attained after 24 hr. was adopted as the final value; subsequent increase of pressure was found to be negligible in an extended experiment.

It was assumed, following Schweitzer and Szebehely (11), that the rate of gas evolution would be proportional to the degree of supersaturation, which in this case was represented

$$\frac{d(\Delta p)}{dt} = k\,(\Delta p_{\infty} - \Delta p)$$

where Δp is the pressure increase at time t, Δp_∞ is the final pressure increase, and k is the rate constant. The integrated equation was written

$$\log \frac{\Delta p_\infty}{\Delta p_\infty - \Delta p} = k't$$

where $2.303\ k' = k$. The rate constants k' were obtained by plotting $\log [\Delta p_\infty/(\Delta p_\infty - \Delta p)]$ against t.

In one set of experiments, the outgassing was allowed to proceed under normal conditions at 30.0°C. for 50 to 60 min. During the next five minutes the bath temperature was lowered to, and maintained at, 27.5°C. (this bath temperature gave a solution temperature of 30.0°C. in the field). At this time the field was turned on and left on until the outgassing was almost complete. The results of a typical experiment are shown in Fig. 1, A; the rate constants k' obtained under a

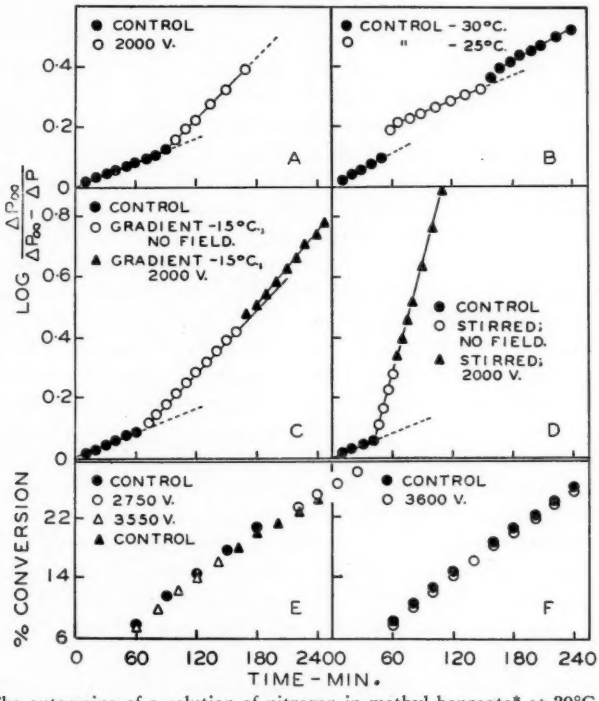

FIG. 1. The outgassing of a solution of nitrogen in methyl benzoate* at 30°C. (A-D), and the polymerization of styrene in bulk at 80°C. (E-F) for the conditions shown. "Control" indicates an unstirred system of uniform temperature in the absence of the field.

variety of conditions are compared in Table I. Exposure of the cell to the laboratory atmosphere prior to filling resulted in a value of 7 for the ratio of the rate constant in the field to the normal rate constant (k'_f/k'_c). Where such exposure

*The results shown in B were obtained when the solution was prepared externally and transferred to the cell under laboratory atmosphere. All other results were obtained when the solutions were prepared in the cell.

TABLE I

A COMPARISON OF k'_c† (NORMAL) AND k'_f† (2000 V.) UNDER VARIOUS CONDITIONS AS NOTED IN COLUMN 1

Condition	k'_c, min.$^{-1}$	Deviation from mean	k'_f, min.$^{-1}$	Deviation from mean	Ratio, k'_f/k'_c
Saturated solution transferred to cell under atmospheric conditions	0.00205	0.00035	0.0143	0.0016	6.98
Saturated solution transferred to evacuated cell under vacuum	0.00145	0.00003	0.00400	0.00033	2.76
Solution in cell at end of 24 hr. experimental period resaturated with N_2 in cell	0.00153	0.00017	0.00336	0.00012	2.20

†*All values of k' are the average of two determinations.*

was prevented the normal outgassing rate was decreased only slightly, but the ratio k'_f/k'_c dropped from 7 to about 2.5.

In a second set of experiments the effects of temperature and stirring were studied. Temperature gradients were produced by sealing the "core" of the cell for the circulation of a second oil at a temperature different from that of the surrounding bath oil. Stirring was accomplished by the introduction of a ring type stirrer of 3 mm. pyrex rod with its shaft extending through the 10/30 standard taper joint. The stirrer was moved up and down by a small electromagnet surrounding a sealed tube fitted to the 10/30 joint.

The results of these experiments are illustrated in Fig. 1, B to D. A decrease in temperature from 30 to 25°C. caused a normal decrease in the outgassing rate, but the rate obtained during a cooling or a heating period was considerably greater than that when the temperature was held constant at either value.This effect was also noticed during the short cooling periods in the earlier experiments. A temperature difference of 15°C. between the cell walls caused an increase in the rate of outgassing roughly equivalent to that of the 2000 volt field, and application of the field under these conditions caused only a very slight further increase (Fig. 1, C). A temperature difference of 25°C. eliminated the effect of the field entirely. Stirring with an oscillation period of 13 sec. increased the rate ninefold and also eliminated the effect of the field (Fig. 1, D). An oscillation period of one second increased the rate 60-fold.

The effect of the field on the bulk polymerization of styrene was reinvestigated with the thermocouple–potentiometer method of temperature measurement. A field of 3600 volts and 1.5 megacycles was used, and the control temperature was set at 80°C. The benzoyl peroxide catalyst concentration used was that corresponding to the maximum effect reported by Bryce *et al.* (1 gm. per liter). A field of about 3600 volts was applied during the later part of one experiment, and during the earlier part of an otherwise similar experiment. As indicated in Fig. 1, E, the field had negligible effect on the polymerization. During the third experiment, the field was applied throughout the course of the polymerization except during the induction period. Fig. 1, F compares the results from this

experiment with those from an otherwise similar one in which no field was used. Again, no field effect is indicated.

DISCUSSION

The Outgassing Process

The results of this investigation are best discussed in terms of a mechanism based on the premise that gas evolution from liquids is dependent on the presence of certain types of nuclei. Foreign particles, microbubbles, and even certain conditions existing in the container walls have been cited as active centers for the process (4, 5, 6, 8).

The mechanism of gas release at a nucleus remains vague, but existing evidence suggests that a nucleus acts as a discontinuity into which dissolved gas can evaporate. The movement of dissolved gas to a nucleus will occur by diffusion in a stagnant system or by a combination of diffusion and mass motion in an agitated system. For a given gas–liquid system at a given temperature, the rate of gas release at a nucleus will be constant, and the rate of the over-all process will depend jointly on the activity of the container wall and the degree of agitation.

In the present study, mechanical stirring increased the rate of gas evolution several-fold, as did also the stirring that resulted from convection currents established by temperature gradients. It is suggested that the increase in rate caused by the electric field was also due to convection currents arising from a temperature gradient. In this case the temperature gradient would result from the absorption of energy from the field, and its subsequent dissipation through the container walls to the bath oil.

This mechanism will explain the results obtained, as follows. For normal outgassing, diffusion would be the main rate controlling process, and differences in wall activity should cause only small differences in the rate of the process. In the field, however, convection would replace diffusion, and the wall activity would become rate controlling. Under these conditions, differences in wall activity should cause much larger differences in the outgassing rate. Hence the small changes in k'_c produced by different methods of filling the cell, and the much larger changes in k'_f (Table I).

There is also the possibility that the field affects the wall activity as a rate controlling factor, either by increasing the activity of the nuclei present, or by creating additional nuclei. If this were the case, however, some field effect should remain even in the presence of mechanical stirring. On the other hand, if the field acts only through the convection currents set up, its effect should become negligible in a sufficiently agitated system. The results of the second set of experiments show that the field had no effect on a well stirred system, nor when a 25°C. temperature difference was maintained across the cell. A slight residual effect remained when the temperature difference was only 15°C.

A comparison of the accelerations caused by field temperature gradients and thermally produced temperature gradients suggests that a field of 2000 volts is roughly equivalent to a temperature difference of 15°C. across the cell, or about 7°C. from the center of the cell to the walls. A temperature difference of this

magnitude may be of great importance in investigations of a kinetic nature.

Kinetic Studies in Alternating Electric Fields

The absorption of energy from an alternating electric field by a liquid in a container, the walls of which are maintained at constant temperature, must result in temperature gradients in the liquid. In the absence of stirring, both conduction and natural convection contribute to transfer of energy from the system.

The kinetics of chemical reactions are normally studied under conditions of a constant uniform temperature throughout the reacting medium. Under these conditions the rate of a reaction of the simple type

$$n\,B \longrightarrow \text{products}$$

is described in terms of the concentration of reactant B by the equation

$$-\frac{dc}{dt} = kc^n \qquad [1]$$

where c is the concentration of reactant B at time t, and k and n are the rate constants and order of the reaction respectively. This integrates to give

$$c = g(c_0, n, k, t) \qquad [2]$$

where g denotes a functional relationship, and c_0 is the concentration of B at zero time. For a liquid system the volume V is essentially constant, and the total quantity of reactant is given by

$$q = \int_V c\,dV = c.V, \qquad [3]$$

whence from [1] and [3]

$$-\frac{dq}{dt} = -V\frac{dc}{dt} = Vkc^n. \qquad [4]$$

In an alternating electric field the temperature is not uniform, but is a function of position. Under these conditions k, which increases with temperature according to the Arrhenius equation

$$k = A\,e^{-E/RT},$$

and c, which is a function of k (equation 2), both vary with position. Equations 1 and 2, therefore, describe the reaction only at some given point in the system, and the over-all reaction must be described by

$$-\frac{dq}{dt} = -\frac{d}{dt}\int_V c^*\,dV = -\int_V \frac{dc^*}{dt}\,dV = \int_V k^*\,c^{*n}\,dV \qquad [5]$$

in which the asterisks denote quantities which vary with position. This expression will be equivalent to equation 4 for the reaction at uniform temperature only if

$$Vkc^n = \int_V k^*\,c^{*n}\,dV, \qquad [6]$$

i.e. only if the uniform temperature T is chosen so that kc^n is equal to $\frac{1}{V}\int_V k^*c^{*n}dV$, the volume average of this expression for the nonuniform temperature.

For a zero order reaction $n = 0$, and the required condition is

$$[7] \qquad k = \frac{1}{V}\int_V k^* dV,$$

or substituting for k using the Arrhenius equation,

$$e^{-E/RT} = \frac{1}{V}\int_V e^{-E/RT^*} dV.$$

Equivalent expressions for the higher order reactions involve t in such a way that the uniform temperature T can be chosen to make the two reactions equivalent only at some instant of time, i.e. it is impossible to choose a constant uniform temperature to ensure thermal equivalence of control and field reactions.

When the temperature range in the field cell is not too great, the task of determining the uniform temperature for the control cell may be simplified by substituting for the Arrhenius equation the linear function

$$k = k_1 + a(T - T_1)$$

where a is a constant, and k_1 and T_1 are corresponding values of the rate constant and temperature at some point within the given range. Substitution for this expression into equation 7 gives

$$T = \frac{1}{V}\int_V T^* dV.$$

Thus control and field reactions will approximate to thermal equivalence provided:

1. The reaction is zero order.
2. The control temperature is the volume average of the temperature in the field.

The effects of stirring and oxygen on the reaction must also be considered if a true field effect is to be isolated. Reactions affected by mixing must be stirred mechanically at a sufficient rate to ensure negligible effect due to convection. In a system capable of reaction with oxygen, the oxygen concentration will depend upon the rate at which it is used up and the rate at which it is absorbed. Schlapfer *et al.* (10) have reported that, even in a practically stagnant column of water, the absorption of air depends mainly upon convection. Such a system will be sensitive to mixing unless an inert atmosphere is used.

It is interesting to recall here the color effect observed in the studies with benzoyl peroxide mentioned previously (9). Although some inhibition of the decomposition of benzoyl peroxide in toluene solution was apparently caused by the field used, an orange color appeared much earlier in the "inhibited" system. The color did not arise when nitrogen was bubbled through the system and it now seems probable that the phenomenon was caused by a more rapid absorption of oxygen under the influence of the field.

The foregoing discussion indicates that the bulk polymerization of styrene should be suitable for investigation in alternating electric fields. It is zero order, and with the fields employed in this study use of the linear expression for k should not lead to serious error. The major problem is the determination of the volume

average temperature in the field. The method used by Bryce *et al.* (2) does not seem adequate because the thermometer bulb was located at the hottest point in the liquid (the top central part). Thus the control reaction took place at a temperature slightly higher than the volume average temperature in the field, and an apparent inhibition resulted. The thermocouple–potentiometer method, however, appears to be more satisfactory. Interaction of the field and thermocouple is prevented by momentarily turning off the field, while the temperature gradient is temporarily eliminated through stirring set up by introduction of the thermocouple, which is immersed to the mid-point. The absence of any field effect under these conditions suggests that the inhibition reported earlier (2) was probably a result of the method used for temperature determinations.

Indeed, neglect of temperature, or the use of improper methods for its determination, might well be responsible for many so-called field effects reported in the literature. Certainly in the absence of a precise description of the methods used for the determination of temperatures, the validity of reports claiming athermal effects produced by alternating electric fields is open to question.

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THE REACTIONS OF ACTIVE NITROGEN WITH BUTENES[1]

By H. Gesser,[2] C. Luner,[3] and C. A. Winkler

ABSTRACT

The reactions of nitrogen atoms with butene-1, *cis*-butene-2, and isobutene at 88°C. and 240°C. were found to produce hydrogen cyanide, propylene, and ethylene as the main products, together with smaller amounts of butane, propane, ethane, methane, and hydrogen. Trace quantities were also obtained of acetylene, a C_5 hydrocarbon, and a mixture, probably of C_6 and C_7 hydrocarbons. The order of reactivities with nitrogen atoms was butene-1> *cis*-butene-2> isobutene. Increased temperature favored the reactions of butene-1 and *cis*-butene-2, but no noticeable increase in reactivity was observed with isobutene.

The reactions of active nitrogen with the lower saturated and unsaturated hydrocarbons have been discussed in previous papers from this laboratory and its marked reactivity attributed to nitrogen atoms (2-5). The reactions of active nitrogen with the butenes appeared to be of particular interest because of the opportunity for studying the effect that the position of the double bond might have on the reactivity of the hydrocarbon molecule in these reactions.

EXPERIMENTAL

The apparatus was essentially similar to that described in the earlier papers. Preliminary experiments showed that hydrogen cyanide was absorbed quantitatively by ascarite (sodium hydroxide on asbestos) with the liberation of water of neutralization. The products of the reaction, after they had been trapped at the temperature of liquid nitrogen, were therefore cycled several times through a previously weighed and evacuated absorption tube containing ascarite, with anhydrous magnesium perchlorate on either side of the ascarite to absorb the liberated water. Hydrocarbon products were estimated by the low temperature distillation and combustion methods used in a previous study (4).

Butene-1, *cis*-butene-2, and isobutene, all of 99% purity, were obtained from the Ohio Chemical Company, Phillips Petroleum, and Polymer Corporation, respectively, and were used after a single bulb to bulb fractionation.

RESULTS AND DISCUSSION

In all experiments, the flow rate of nitrogen was 1.17×10^{-4} mole per sec., and the pressure in the system was 1.7 mm. of mercury.

The results are plotted in Fig. 1. The yields of methane and hydrogen were small and erratic, and varied from 0.1×10^{-6} to 0.5×10^{-6} mole per sec. and from 1×10^{-6} to 3×10^{-6} mole per sec. respectively. Acetylene, a C_5 hydrocarbon fraction, and a higher boiling fraction (surmised to be a mixture of C_6 and C_7 hydrocarbons) were obtained in trace quantities. The carbon balance showed an extreme variation from 96% to 104%, with an average value of 99.7%. The average hydrogen balance was 95%.

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[2] *Holder of a National Research Council Studentship.*
[3] *Holder of Quebec Provincial Scholarships, 1948-51.*

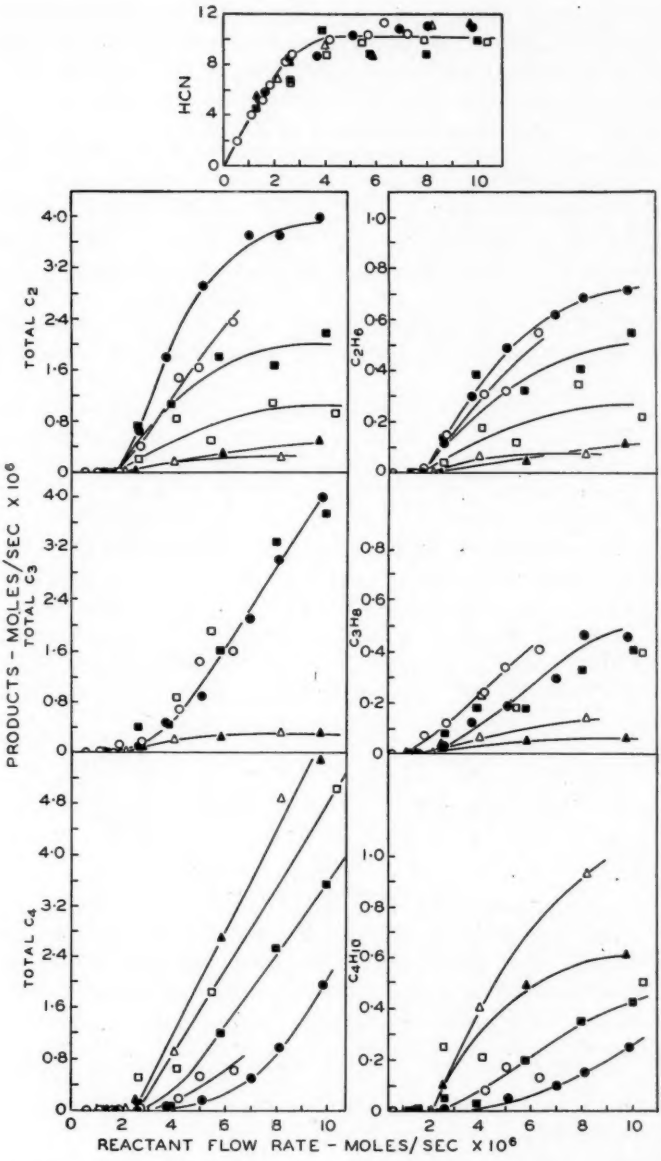


FIG. 1. Rate of formation of various products in the nitrogen atom – butene reactions.

Reactant	Temp. = 88°C.	Temp. = 240°C.
Butene-1	○	●
cis-Butene-2	□	■
Isobutene	△	▲

The yields of hydrogen cyanide (Fig. 1) show that, at hydrocarbon flow rates above about 4×10^{-6} mole per sec., the butenes reacted to consume completely the available nitrogen atoms. At lower hydrocarbon flow rates the mole ratio of hydrogen cyanide produced to hydrocarbon consumed was about 4 : 1. The maximal yield of hydrogen cyanide was $10 \pm 1 \times 10^{-6}$ mole per sec.; this value may be compared with an average atom flow rate of $15 \pm 3 \times 10^{-6}$ mole per sec. as determined by measurements with the Wrede gauge.

Previous studies of the reaction of nitrogen atoms with hydrocarbons have shown that unsaturated hydrocarbons are much more reactive with nitrogen atoms than saturated hydrocarbons. It has previously been suggested, and the suggestion supported by rather convincing argument, that the point of attack of the nitrogen atom is the double bond, with the formation of a collision complex. It would therefore be expected that the butenes would behave in a similar manner.

The absence of significant yields of higher hydrocarbons in the ethylene–nitrogen atom reaction (3, 5) and in the propylene – nitrogen atom reaction (4), and the formation of only trace quantities of C_5 and higher hydrocarbons in the present reactions, makes it reasonable to assume that the propylene formed is a primary hydrocarbon product in the reaction of nitrogen atoms with the butenes.

For butene-1, the primary reaction step may be represented as follows:

$$CH_3CH_2CH = CH_2 + N \rightarrow \left[CH_3CH_2\underset{\diagdown\,N\,\diagup}{CH}\text{–}CH_2 \right] \rightarrow CH_3CH_2\dot{C}H: + H + HCN \qquad [1]$$

The propylidene radical, by analogy with the ethylidene radical, might be expected to rearrange immediately to propylene.

$$\dot{C}H_3CH_2CH: \rightarrow CH_3CH = CH_2 \qquad [2]$$

For isobutene the primary reaction step may be represented as:

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!C = CH_2 + N \rightarrow \left[\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!\overset{\diagdown\,N\,\diagup}{C} - CH_2 \right] \rightarrow \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!\dot{C}: + HCN + H \qquad [3]$$

$$CH_3\ddot{C}CH_3 \rightarrow CH_3CH = CH_2 \qquad [4]$$

Reaction [4] is reasonable since Bawn and Dunning (1) found that sodium atoms react with 2,2-dibromopropane with weak chemiluminescence which was associated with a hydrogen shift, probably due to the following reactions:

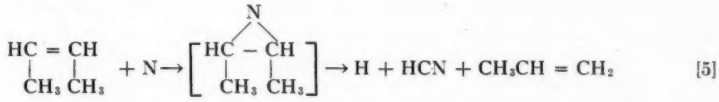
$$CH_3CBrCH_3 + Na \rightarrow CH_3\ddot{C}CH_3 + NaBr$$

$$CH_3\ddot{C}CH_3 \longrightarrow CH_3CH = CH_2 + h\nu$$

Hence the isopropyl diradical apparently does not have an appreciable life and rearranges to propylene immediately upon formation.

The primary reaction step for *cis*-butene-2 with nitrogen atoms to yield propylene cannot consist of a simple rupture at the double bond since this would result in the formation of ethylene as one of the primary products. It is therefore suggested that the nitrogen atom reacts with *cis*-butene-2 at the double bond to form a collision complex of the same type as that formed with other olefins, but

that a rearrangement within the complex occurs simultaneously with ejection of a secondary hydrogen atom and dissociation of the complex into hydrogen cyanide and propylene.



[5]

The propylene formed in all three butene reactions might be considered to undergo further reactions with nitrogen atoms in the manner suggested by Trick and Winkler (4) to form ethylene, which in turn may further react with nitrogen atoms to form methylene radicals.

Reactions [1], [3], and [5] indicate that hydrogen atoms are a primary product of the reactions of nitrogen atoms with the butenes. The parallel trends in total and in saturated hydrocarbon products seem to indicate that the most important reaction leading to the formation of the saturated compounds is hydrogenation of the corresponding unsaturated hydrocarbon.

Acetylene, in the trace amounts observed, is probably formed from the dehydrogenation of ethylene by hydrogen atoms, while the methane formed may be adequately accounted for by hydrogenation of methylene radicals.

It is inherent in the proposed mechanisms that for every molecule of hydrogen cyanide formed, one atom of hydrogen is produced. Since the rate of production of hydrogen cyanide is constant, beyond the butene flow rate corresponding to complete nitrogen atom consumption, the rate of formation of hydrogen atoms in this region is also constant. Hence at high flow rates of butene, it would be expected that the yields of the saturated products should be constant if they are formed as postulated. This conforms, in general, to the observed behavior. However, only about one-quarter of the atomic hydrogen produced is used to form saturated products and methane. This is probably due to the competitive recombination reaction of hydrogen atoms, by a three-body collision with a nitrogen molecule;

$$H + H + N_2 \quad \rightarrow \quad H_2 + N_2.$$

This reaction appears to be almost independent of flow rate of butene, probably because of the large excess of nitrogen molecules in the reaction mixture.

The tendency for the curves of total C_2 hydrocarbon to level off is probably due to the fact that consecutive steps are involved in the reaction. Thus if the nitrogen atoms are in excess, the propylene formed in the primary reaction can further react to form ethylene. However if the butenes were in sufficiently great excess, essentially all the nitrogen atoms may be expected to be consumed by the primary reaction step to form only propylene and no ethylene. Hence the C_2 curves should show a maximum, and decrease to zero at sufficiently large carbon–nitrogen atom ratios. In practice it was impossible to work at the high butene flow rates necessary to realize such a maximum experimentally.

Most of the C_4 hydrocarbon is unreacted butene in both reactions. With isobutene there is practically no change in amount of C_4 hydrocarbon recovered as the temperature is increased (i.e. amount of isobutene reacted remains essentially

constant), while with butene-1 and *cis*-butene-2 the amount of C_4 hydrocarbon decreased significantly with increase of temperature (i.e. the amounts of butene-1 and *cis*-butene-2 reacted increased significantly). This would indicate that the activation energy for the reaction of isobutene with nitrogen atoms is somewhat less than for the analogous reactions of butene-1 and *cis*-butene-2. It would seem necessary, then, to attribute the lower rate of the isobutene reaction to a smaller steric factor.

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SYNTHESIS OF ORGANIC DEUTERIUM COMPOUNDS
PART VI. FORMALDEHYDE-d_2 AND FORMALDEHYDE-d[1]

By R. A. B. Bannard[2], A. T. Morse[3], and L. C. Leitch[3]

ABSTRACT

Formaldehyde-d_2 was prepared in 62.5% over-all yield from 1,2-dibromoethane-d_4 via the corresponding glycol diacetate and glycol. Formaldehyde-d was prepared by the same method from *sym*-1,2-dibromoethane-d_2. From the high isotopic purity of the deuterated formaldehydes obtained, it has been definitely established that it is a pair of hydrogen atoms from the hydroxylic groups of the glycols that generates acetic acid during dialdehyde fission with lead tetraacetate. The densities and refractive indices of the deuterated ethylene glycol diacetates and ethylene glycols used as intermediates in the synthesis of the deuterated formaldehydes have been determined.

INTRODUCTION

This investigation was undertaken to obtain a quantity of formaldehyde-d_2 which was required by Steacie and co-workers (25) for use in the study of hydrogen abstraction reactions. A synthetic method was required which would provide formaldehyde-d_2 of maximum deuterium content in a physical state from which the monomer could be readily generated for use in photochemical reactions. Further, it was desirable that the over-all yield be high, that the starting material be readily available in a high state of isotopic purity, and that intermediates should not be prone to loss of deuterium by exchange reactions during manipulation.

In 1938 Ebers and Nielsen (7) prepared formaldehyde-d_2 by irradiating a mixture of carbon monoxide and deuterium in a quartz mercury arc, but gave no experimental details. The formaldehyde-d_2 thus obtained was contaminated with glyoxal and required considerable purification before it could be used in spectroscopic studies (7). It was therefore considered that this method of preparation would not be suitable for the present investigation.

It was reported by Klar (17) that both hydrogen atoms in formaldehyde are readily exchangeable by the reaction shown in Equation 1.

$$CH_2O + D_2O \rightleftarrows CD_2O + H_2O \qquad [1]$$

Subsequently, Wirtz and Bonhoeffer (31) found that this exchange process does not occur even in the presence of acidic or alkaline catalysts after several months' equilibration. The latter results were confirmed by Waters (30) who obtained α-polyoxymethylene containing no deuterium by polymerization of formaldehyde in deuterium oxide under either acidic or alkaline conditions.

The availability of paraformaldehyde by the catalytic oxidation of methanol (27, pp. 1–17) has made unnecessary, heretofore, the development of laboratory methods for the direct synthesis of anhydrous formaldehyde. Application of the catalytic method to the preparation of formaldehyde-d_2 was excluded because the necessary deuteromethanol is not readily available.

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The thermal decomposition of metallic formates to either methanol or formaldehyde was extensively studied before the successful application of the high pressure methanol synthesis (21). The best yield of formaldehyde was obtained from stannous formate which decomposed at 180° C. according to Equation 2 (9).

$$3(H\text{–}\overset{\overset{O}{\|}}{C}\text{–}O)_2Sn \xrightarrow{\Delta} CH_2O + HCOOCH_3 + 3SnO + 3CO_2 \qquad [2]$$

Some formaldehyde-d_2 was obtained by this method in the present work. However, yields were not sufficiently high to warrant a detailed study because, according to Equation 2, at least two-thirds of the deuterium initially employed would be converted to methyl-d_3 formate-*d*.

Some interest has recently arisen in the synthesis of formaldehyde-C^{14}. Jones and Skraba (15) subjected methanol-C^{14} to acetylation with acetyl chloride to form methyl-C^{14} acetate. Chlorination and hydrolysis of the latter substance followed by dilution with carrier formalin gave, on distillation, paraformaldehyde containing paraformaldehyde-C^{14}. Cox and Warne (3) have more recently prepared formaldehyde-C^{14} in aqueous solution by oxidative fission of ethylene-C^{14} glycol with sodium bismuthate.

A serious objection to the application of the two foregoing methods is that the formaldehyde-C^{14} is obtained as a dilute aqueous solution. According to Walker (27, pp. 58–63), the isolation of monomeric formaldehyde from aqueous solutions by distillation is not realizable in practice, although it is theoretically possible. Under the best conditions of formaldehyde recovery, the end product is paraformaldehyde containing 7% combined water (13). Isolation via derivatives might be helpful in effecting concentration without substantial loss but regeneration of the formaldehyde by hydrolysis would still necessitate isolation as paraformaldehyde. To obtain good yields of anhydrous formaldehyde it would first be necessary to prepare alkali-precipitated α-polyoxymethylene from the paraformaldehyde (28). The yield in this step is, at best, only 58% of theoretical (24). The conversion of alkali-precipitated α-polyoxymethylene to anhydrous monomeric or polymeric formaldehyde has been elaborated by Walker (28). These considerations made any synthetic method in which formaldehyde-d_2 is generated in aqueous solution appear most unattractive and expensive. It was, therefore, considered essential to develop a method which would produce directly formaldehyde in an anhydrous condition.

The cleavage of ethylene glycol to two moles of formaldehyde can be carried out nearly quantitatively. Reagents which must be used in aqueous solution, such as periodic acid (14, 19), sodium bismuthate (10, 22, 3), the unstable trivalent silver ion (10), and chromyl chloride (23), were ignored because of the difficulty of obtaining a good yield of anhydrous formaldehyde from the resulting solution (see above). Hence attention was centered on the use of lead tetraacetate in organic solvents (4, 5).

In a recent patent, Drewitt (6) claims to have obtained almost quantitative yields of formaldehyde by mixing red lead, glacial acetic acid, and ethylene glycol

at room temperature, followed by heating at 60–70° C. with vigorous stirring until the red lead dissolved. Experiments were performed according to Drewitt's directions but in no case was monomeric formaldehyde isolated by heating the resultant solution under reflux with adequate facilities for condensing volatile effluent gases. It was possible to isolate small amounts of formaldehyde polymer on fractionation of the solution, but the yields were too low (15%) to warrant further study of the method. Drewitt's claim (6) must refer to the yield of formaldehyde in solution, available for reaction, but not isolable as anhydrous formaldehyde.

Hockett and co-workers (12) obtained formaldehyde from the carbohydrate "arlitan" by a technique in which the carbohydrate, dissolved in a small quantity of glacial acetic acid, was added to dry lead tetraacetate. The formaldehyde was swept out of the reaction system by heating the mixture under reflux in a slow current of dry air. The effluent gases were adsorbed in an acidic 2,4-dinitrophenylhydrazine solution, and the quantity of formaldehyde evolved estimated as the 2,4-dinitrophenylhydrazone. By this method 62% of the theoretical yield of formaldehyde was obtained. Control experiments were also performed using ethylene glycol as substrate. The yield of formaldehyde was not reported in this instance but the authors state that the procedure and apparatus are not wholly satisfactory (12). Acetic acid is known to form loose addition compounds with formaldehyde which are probably monoesters of methylene and polyoxymethylene glycols (27, p. 191). Furthermore, solutions of formaldehyde in hydroxylic solvents do not evolve formaldehyde quantitatively on heating (28). However, solutions of formaldehyde in nonhydroxylic solvents evolve monomeric formaldehyde gas almost quantitatively on warming to room temperature (27, p. 28). Evidently, maximum yields of formaldehyde from ethylene glycol by oxidative cleavage with lead tetraacetate would most probably be realized in a nonhydroxylic solvent. Benzene was selected as solvent because it can be readily dried and dissolves lead tetraacetate more readily than most other nonhydroxylic solvents (5).

Glycol cleavage with lead tetraacetate proceeds only if the hydroxyl groups of the glycol are unsubstituted (5). It was logical to conclude from this observation that the two hydrogen atoms lost from the glycol during dialdehyde cleavage, which appear ultimately as acetic acid, are hydrogen atoms originally bound to oxygen rather than to carbon. This view is in agreement with that of Waters (29), who considers that primary attack by the lead tetraacetate is at a hydroxylic and not a carbon-bound hydrogen atom. It was therefore not considered necessary to prepare ethylene-d_4 glycol-d_2 as starting material for the synthesis of formaldehyde-d_2, because two deuterium atoms would merely be lost as acetic acid-d during dialdehyde cleavage. Attention was therefore turned to the synthesis of ethylene-d_4 glycol.

1,2-Dibromoethane-d_4 (I) was chosen as starting material for the preparation of ethylene-d_4 glycol, since it was readily available in a high state of isotopic purity by the method of Leitch and Morse (18). The synthetic scheme is shown in Equations 3, 4, and 5.

$$\begin{array}{l} CD_2Br \\ | \\ CD_2Br \end{array} + 2CH_3COOK \rightarrow \begin{array}{l} CD_2OCOCH_3 \\ | \\ CD_2OCOCH_3 \end{array} + 2KBr \qquad [3]$$

I II

$$\begin{array}{l} CD_2OCOCH_3 \\ | \\ CD_2OCOCH_3 \end{array} + 2C_2H_5OH \xrightarrow{Na} \begin{array}{l} CD_2OH \\ | \\ CD_2OH \end{array} + 2CH_3COOC_2H_5 \qquad [4]$$

III

$$\begin{array}{l} CD_2OH \\ | \\ CD_2OH \end{array} + Pb(OCOCH_3)_4 \rightarrow 2CD_2O + Pb(OCOCH_3)_2 + 2CH_3COOH \qquad [5]$$

IV

Pilot experiments were first performed with undeuterated substances to establish the range of yields to be expected for the syntheses with deuterated compounds to be undertaken later.

Ethylene glycol diacetate was prepared in 88.5% yield by the action of fused potassium acetate on 1,2-dibromoethane, using a modification of the method of Henry and Henry (11). The use of silver acetate in this reaction gave greatly reduced yields (32). Ethylene glycol diacetate was converted to ethylene glycol in 93.0% yield by a modification of the transesterification procedure of Bainbridge (1). An attempt to obtain ethylene glycol from 1,2-dibromoethane by oxidation with silver oxide was unsuccessful. This result agrees with the previous observations of Beilstein and Wiegand (2). Formaldehyde was prepared in 80% yield by cleavage of the ethylene glycol with lead tetraacetate in benzene suspension heated under reflux. The product was obtained first as anhydrous gas which was condensed, distilled *in vacuo*, and redistilled *in vacuo* into anhydrous ether. The formaldehyde dissolved in the ether polymerized slowly to eu-polyoxymethylene on standing at 0° C. in a sealed tube for three days. The over-all yield of formaldehyde, based on 1,2-dibromoethane, was 66%.

Difficulty was at first experienced with the polymerization step and several explosions resulted by allowing the trap containing formaldehyde solution in ether to warm too rapidly (16). This hazard was at first overcome by conducting the polymerization in ether at −80° C. with addition of *n*-butylamine as polymerization catalyst (28). It was found, however, that the polymer thus obtained could not be depolymerized by heating *in vacuo*. Consequently, addition of the polymerization catalyst was omitted in subsequent preparations in favor of polymerization at 0° C.

In a similar manner *sym*-1,2-dibromoethane-d_2 was converted to *sym*-ethylene-d_2 glycol diacetate in 90.0% yield. Transesterification of the latter substance gave 81.5% of *sym*-ethylene-d_2 glycol, oxidative cleavage of which produced formaldehyde-*d* as anhydrous polymer in 76% yield.

1,2-Dibromoethane-d_4 (I) was converted to ethylene-d_4 glycol diacetate (II) in 94.0% yield, transesterification of which produced an 88.5% yield of ethyl-

ene-d_4 glycol (III). Oxidative cleavage of the latter substance produced a 75% yield of formaldehyde-d_2 (IV) as anhydrous polymer.

The fact that the yield of formaldehyde is not quantitative by the method elaborated in this paper may be readily explained by the assumption that some formaldehyde is retained in solution by the acetic acid which is generated in accordance with Equation 5. The lower yields which Hockett and co-workers obtained (12) seem to substantiate this view. It was noted that the residual benzene solution possessed a definite odor of formaldehyde even after prolonged boiling to the point where no further liquid formaldehyde was being condensed by the cooling system. The same phenomenon was observed in the unsuccessful attempts to evolve monomeric formaldehyde by oxidative fission in acetic acid media. A quantitative yield of monomer could only be realized by neutralizing the acetic acid as it is generated. The basic substance used for this purpose must not promote the irreversible polymerization of the monomer.

The isotopic purity of the deuterated 1,2-dibromoethanes used as starting materials was determined by mass spectrometer analysis, whereas the isotopic purity of the deuterated formaldehydes was established by conversion to deuterated methylene chlorides, followed by mass spectrometer analysis. Since the isotopic purity of the formaldehyde-d_2 exceeded 98%, it is evident that it is the hydroxylic hydrogen atoms of the glycol which are eliminated as acetic acid during oxidative fission with lead tetraacetate.

The deuterium content of the deuterated ethylene glycol diacetates and ethylene glycols could not be determined by their mass spectra. However, the densities and refractive indices of the deuterated substances in relation to the same physical constants for the undeuterated compounds should serve as an indication of isotopic purity. McLean and Adams (20) developed an equation by means of which the densities of deuterated organic compounds can be calculated if the extent of deuterium substitution and density of the ordinary compound are known. Table I shows the observed densities for the deuterated

TABLE I

DENSITIES AND REFRACTIVE INDICES OF ETHYLENE GLYCOL DIACETATES AND ETHYLENE GLYCOLS

Compound	Refractive index, n_D^{20}	Density, d_4^{20}	
		Calculated	Found
Ethylene glycol diacetate	1.4154		1.1051; 1.1052
sym-Ethylene-d_2 glycol diacetate	1.4150	1.1204	1.1210; 1.1211
Ethylene-d_4 glycol diacetate	1.4147	1.1356	1.1372; 1.1371
Ethylene glycol	1.4313		1.1137; 1.1135
sym-Ethylene-d_2 glycol	1.4302	1.1496	1.1507; 1.1505
Ethylene-d_4 glycol	1.4293	1.1858	1.1895; 1.1894

ethylene glycol diacetates and ethylene glycols in relation to those calculated by McLean and Adams' equation. The refractive indices of the compounds are also given in this table.

In Table I it is noted, as would be expected, that the densities increase progressively as the degree of substitution of deuterium for hydrogen increases. The effect of deuterium substitution on the densities of the glycols is much greater per deuterium atom introduced than in the case of the glycol diacetates because of the much higher molecular weights of the latter substances.

The densities found agree well with the calculated values in the case of the d_2 compounds but not for the d_4 compounds. In all cases the observed densities exceed the calculated values. These results differ from those of McLean and Adams (20) who found that where the observed and calculated values were in poor agreement, the calculated always exceeded the observed. The discrepancies were attributed to one of two causes (20). Either the deuterated compounds were not of sufficiently high isotopic purity, or the fundamental assumption that the molecular volumes of hydrogen and deuterium in organic compounds are identical—made by McLean and Adams in developing their equation—was invalid, and that the molecular volumes of deuterated compounds must exceed those of nondeuterated compounds. In the light of the results of the present investigation both of these explanations appear inadequate since the error is in the wrong direction. It is certain, however, that such calculations cannot be relied upon as an absolute measure of isotopic purity, and further studies along this line are necessary to determine the cause of the discrepancies.

EXPERIMENTAL

Ethylene Glycol Diacetate

Sixty gm. (0.612 mole) of fused potassium acetate, 63.0 gm. (0.335 mole) of 1,2-dibromoethane, and 19 cc. of glacial acetic acid were mixed in a 500 cc. round-bottomed flask fitted with a reflux condenser protected by a calcium chloride drying-tube. The mixture was heated under reflux for three hours, after which the liquid portion was removed by distillation, first at atmospheric pressure (60 cc.) and finally at 20 mm. pressure (2 cc.). The distillate was transferred to a 500 cc. round-bottomed flask containing 80.0 gm. (0.816 mole) of fused potassium acetate and 60.0 gm. (0.309 mole) of 1,2-dibromoethane. The mixture was heated under reflux for three hours, following which the liquid portion was distilled as described above, yielding 100 cc. of distillate at atmospheric pressure and a further 3.7 cc. at 20 mm. pressure. The combined distillates were fractionated at atmospheric pressure and the fraction of b.p. 182–188° C. (mostly at 186–188° C.) was retained. The column and pot residue were extracted with anhydrous ether, and the extract combined with the above-mentioned fraction. The resultant solution was fractionated *in vacuo* yielding 84.5 gm. (88.5%) of colorless liquid, b.p. 91–93° C. at 23 mm.; n_D^{20} 1.4154; d_4^{20} 1.1051, 1.1052. Taylor and Rinkenbach (26) report the refractive index of ethylene glycol diacetate as n_D^{20} 1.4150.

sym-Ethylene-d_2 Glycol Diacetate

The procedure was the same as for the preparation of ethylene glycol diacetate except that 50.0 gm. (0.263 mole) of *sym*-1,2-dibromoethane-d_2, 59.0 gm. (0.602 mole) of fused potassium acetate, and 8 cc. of glacial acetic

acid were used. Ethylene-d_2 glycol diacetate was obtained as a colorless liquid (35.0 gm.; 90.0%) b.p. 185–188° C.; n_D^{20} 1.4150; d_4^{20} 1.1210, 1.1211. The *sym*-1,2-dibromoethane-d_2 used in this preparation was found to contain 95.5 mole % $C_2D_2H_2Br_2$ by mass spectrometer analysis.

Ethylene-d_4 Glycol Diacetate

The procedure was the same as for the preparation of ethylene glycol diacetate except that 51.0 gm. (0.265 mole) of 1,2-dibromoethane-d_4, 59.0 gm. (0.602 mole) of fused potassium acetate, and 8 cc. of glacial acetic acid were used. Ethylene-d_4 glycol diacetate was obtained as a colorless liquid (37.4 gm.; 94.0%), b.p. 186–188° C.; n_D^{20} 1.4147; d_4^{20} 1.1372, 1.1371. The 1,2-dibromoethane-d_4 used in this preparation was found to contain 97.9 mole % $C_2D_4Br_2$ by mass spectrometer analysis.

Ethylene Glycol

A sodium ethoxide solution was prepared—from 0.5 gm. of sodium and 200 cc. of absolute ethanol—in a 500 cc. round-bottomed flask equipped with a reflux condenser protected by a calcium chloride drying tube. A solution of 43.8 gm. (0.300 mole) of ethylene glycol diacetate in 100 cc. of absolute ethanol was added at room temperature to the sodium ethoxide solution, and the resultant solution heated under reflux for six hours. The ethyl acetate and most of the ethanol were removed by distillation at atmospheric pressure. The residue was transferred to a 50 cc. modified Claisen flask and fractionated *in vacuo* when 17.3 gm. (93.0%) of ethylene glycol was obtained as a colorless liquid; b.p. 99–104° C. at 22–23 mm.; n_D^{20} 1.4313; d_4^{20} 1.1137, 1.1135. Gallaugher

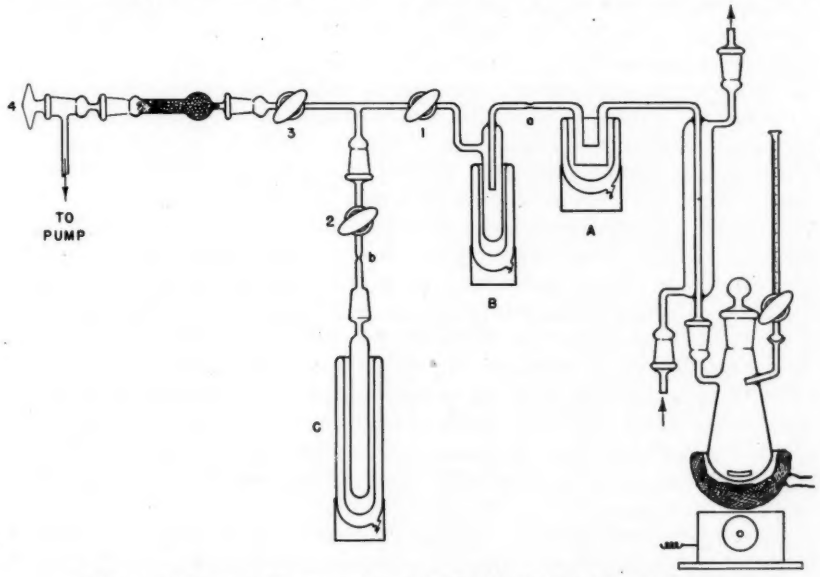

FIG. 1. Apparatus for preparation of formaldehyde-*d* and formaldehyde-d_2.

and Hibbert (8) report the refractive index of ethylene glycol as n_D^{20} 1.4314.

sym-Ethylene-d_2 Glycol

The procedure was the same as for the preparation of ethylene glycol except that 29.0 gm. (0.196 mole) of *sym*-ethylene-d_2 glycol diacetate, 240 cc. of absolute ethanol, and 0.6 gm. of sodium were used. *sym*-Ethylene-d_2 glycol was obtained as a colorless liquid (10.2 gm.; 81.6%); b.p. 86–87° C. at 8 mm.; n_D^{20} 1.4302; d_4^{20} 1.1507; 1.1505.

Ethylene-d_4 Glycol

The procedure was the same as for ethylene glycol except that 35.5 gm. (0.236 mole) of ethylene-d_4 glycol diacetate, 250 cc. of absolute ethanol, and 0.5 gm. of sodium were used. Ethylene-d_4 glycol was obtained as a colorless liquid (13.8 gm.; 88.5%) b.p. 86–87° C. at 8 mm.; n_D^{20} 1.4293; d_4^{20} 1.1895, 1.1894.

Formaldehyde

The apparatus was assembled as shown in Fig. 1. Lead tetraacetate, 56 gm. (0.12 mole) was placed in the reaction flask and the system evacuated to 0.05 mm. pressure for 30 min. while the apparatus was heated gently with a bare flame to remove moisture. Dry air was introduced through stopcock No. 4 and 200 cc. of anhydrous reagent benzene was added via the burette. Stirring was begun, water at 0° C. was circulated through the condenser, traps 1 and 2 were immersed in dry ice and acetone, and the mixture was heated under gentle reflux. Ethylene glycol, 6.2 gm. (0.10 mole), was added dropwise over a 15 min. period by means of the burette. During this period, the originally dark brown mixture became pale yellow and a white precipitate of lead diacetate separated. Simultaneously, liquid formaldehyde collected in trap A, and formaldehyde polymer appeared on the upper walls of the condenser and delivery tube leading to trap A. The burette was rinsed with 10 cc. of anhydrous reagent benzene, and the mixture was heated under reflux with stirring for a further hour. The reaction vessel was cooled in an ice bath, and the formaldehyde polymer which had formed on the upper walls of the flask depolymerized by gentle heating with a bare flame. The reaction flask was disconnected, the lower end of the condenser closed by means of a cap, trap B immersed in liquid nitrogen, and stopcock No. 1 shut. The system was evacuated to 0.1 mm. pressure, and stopcock No. 1 opened very slowly to minimize loss of formaldehyde during evacuation of the remainder of the system to 0.1 mm. pressure. Stopcock No. 1 was shut and the liquid formaldehyde distilled into trap B by allowing trap A to warm slowly after removal of the dry ice and acetone from the latter. The rate of distillation was controlled by occasional immersion of trap A in dry ice and acetone. After the liquid formaldehyde had distilled, the condenser jacket was heated with nitrobenzene under reflux to depolymerize the formaldehyde polymer which had collected on the walls. At the same time, trap A and the delivery tube leading to trap B was heated gently with a bare flame for the same purpose. Trap B was sealed off at constriction *a*. Trap C, containing 20 cc. of anhydrous reagent ether, was connected to the system, evacuated to 0.1 mm. pressure. Stopcock No. 3 was shut, the ether allowed to melt, then

trap C was cooled in dry ice and acetone. The formaldehyde was distilled into trap C after opening stopcock No. 1. Trap C was sealed off at constriction *b*. The trap was kept overnight in dry ice and acetone at −78° C., throughout the following day at −25 to −10° C., then for three days at 0° C. during which time the polymer separated as a white flocculent solid. The trap was cooled once more in dry ice and acetone, opened, inserted on a vacuum line and evacuated. The ether was distilled slowly from the polymer into another trap immersed in liquid nitrogen. Distillation of ether was continued until the trap containing the formaldehyde polymer was at 35° C. Formaldehyde, 4.8 gm. (80%), was thus obtained as a colorless polymeric powder. Found % CH_2O; 100.1; 99.8%.

Formaldehyde-d

sym-Ethylene-d_2 glycol (6.2 gm.; 0.10 mole) was oxidized in exactly the same manner. Formaldehyde-*d*, 4.65 gm. (75%), was obtained as colorless polymer, which on treatment with phosphorus pentachloride gave methylene-*d* chloride of the following composition, as determined by mass spectrometer analysis:

$$93.3 \pm 0.2 \text{ mole \% } CHDCl_2.$$

These figures establish that the formaldehyde-*d* also contains 93.3 ± 0.2 mole % CHDO.

Formaldehyde-d_2

Formaldehyde-d_2 was prepared in 76% yield (4.8 gm.) from 6.5 gm. (0.098 mole) of ethylene-d_4 glycol by the same method as described for formaldehyde. The colorless polymer was converted into methylene-d_2 chloride. Mass spectrometer analysis of the chloro-compound gave the following composition: 97.0 mole % CD_2Cl_2; 2.7 mole % $CHDCl_2$. The formaldehyde-d_2 therefore contains 97.0 mole % CD_2O (98.3 atom % D).

ATTEMPTED ISOLATION OF FORMALDEHYDE MONOMER BY GLYCOL CLEAVAGE IN GLACIAL ACETIC ACID

Seventy-five gm. (0.11 mole) of red lead, 250 gm. of glacial acetic acid, and 6.2 gm. (0.10 mole) of ethylene glycol were mixed in the reaction flask of the formaldehyde generator shown in Fig. 1 and heated with mechanical stirring at 60–70° C. for 30 min. until the red lead had dissolved. The solution was heated under reflux for a further 30 min. but no liquid formaldehyde collected in the traps, and only an insignificant amount of polymeric formaldehyde collected at the lower end of the condenser. The solution possessed a strong odor of acetic acid, but the pungent odor of formaldehyde was also perceptible. The solution was fractionated at atmospheric pressure, but although the formaldehyde concentrated in the heads fraction of b.p. 101–115° C., as shown by the strong odor of formaldehyde which this fraction possessed, no separation of polymer occurred.

A second experiment was performed as described for the preceding experiment, except that 56.5 gm. (0.125 mole) of lead tetraacetate was used instead of the red lead, and the ethylene glycol was added dropwise. No liquid for-

maldehyde was obtained on heating the solution under reflux, but on fractionation of the solution, polymeric formaldehyde separated from the fraction of b.p. 100–114° C. on standing. The polymer was collected by filtration and washed with 25 cc. of anhydrous ether. Weight, 0.9 gm. (15.0%).

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A KINETIC STUDY OF THE HYDROLYSIS OF BENZALANILINE[1]

By A. V. Willi[2] and R. E. Robertson

ABSTRACT

The rates of the acid catalyzed hydrolysis of a series of para substituted benzalanilines have been studied in 50/50 methanol–water in the presence of acetate buffers. Special and general acid catalysis were observed. The effect of para substituents on the rate is different for the charged and uncharged catalyst, and Hammett's relation cannot be applied. Similarly the effect of substituents on the Arrhenius constants for the two cases is different. The para dimethylamino derivative provides an interesting special case. For low buffer concentrations and in unbuffered solutions certain deviations were observed which show that the dependence of the rate on the catalyst concentration is more complicated than the equation

$$k = k_{H^+} \times [H^+] + k_{HAc} \times [HAc]$$

INTRODUCTION

In a study of the hydrolysis of benzalanilines reported by Porai-Koshits and co-workers (4) the effects of certain para substituents seemed so unusual as to warrant reinvestigation. That work was done in water, in the presence of strong acids, the reaction being followed by titration methods. A more convenient method was available to us since the ultraviolet absorption of benzalaniline, in the region of 320–350 mμ, is much larger than for a mixture of benzaldehyde and aniline (Fig. 1). By this means, a kinetic study of the acid catalyzed hydrolysis of benzalaniline and some para substituted derivatives with Me, MeO, Cl, NO_2, and $(CH_3)_2N$ was carried out. Because it was found that the solubility of these substances was too low in pure water, a

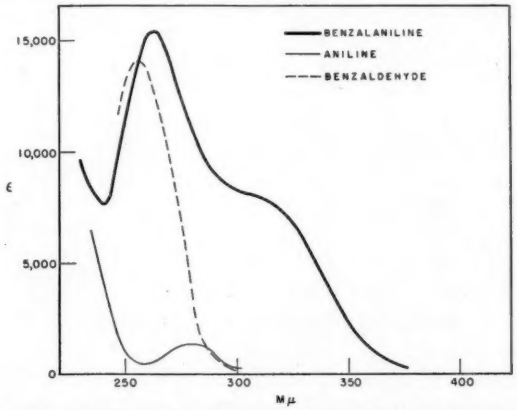


Fig. 1. Absorption spectra of benzalaniline, aniline, and benzaldehyde.

[1] *Manuscript received in original form July 15, 1952, and as revised, December 15, 1952. Contribution from the Division of Pure Chemistry, National Research Laboratories, Ottawa. Issued as N.R.C. No. 2940.*

This paper was presented at the Buffalo meeting of the American Chemical Society, before the Physical and Inorganic Chemistry Division, program No. 29, in March, 1952.

[2] *National Research Laboratories Postdoctorate Fellow, 1950-52, Division of Pure Chemistry.*

50/50 w/w methanol–water mixture was used as a solvent. In contrast to the findings of Porai-Koshits and co-workers, we found that benzalaniline hydrolyzed far too rapidly for measurement in strong acids at room temperature. It is probable that these workers were following the rate of solution rather than the rate of hydrolysis. Convenient rates were obtained, however, at lower hydrogen ion concentrations. This paper gives a preliminary report on our findings in acetate buffers at constant ionic strength and in unbuffered solutions. It will be apparent, however, that further measurements will be necessary to establish the detailed mechanism.

EXPERIMENTAL

The kinetic cell of 380 ml. contained a circulating stirrer which both mixed the solution and forced circulation through a quartz cell (1 cm.^{2} cross section, with plane faces) which was held in the normal position in a Model DU Beckman Spectrophotometer (Fig. 2). The cell was thermostated to within $\pm 0.03°$ C. A quartz reference cell was attached to the kinetic cell; the whole was fixed on a frame mounted on an optical bench in such a fashion that the absorption of either the kinetic or reference cell could be measured conveniently.

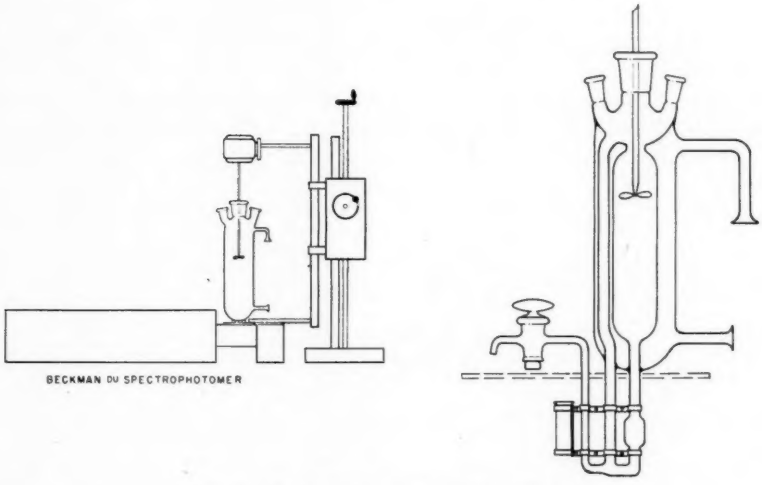


FIG. 2. Kinetic apparatus and reaction cell.

In measuring a reaction, the cell was filled with the requisite buffer solution and permitted to reach temperature equilibrium. After one-half hour the required amount of the benzalaniline was quickly added in a methanol solution with a 2 ml. hypodermic syringe. After 90 sec. absorption measurements were begun with either the normal Beckman DU Photometer or, in the case of fast runs, by substituting an IP28 Photomultiplier and an Esterline Angus recorder.

Rates were determined from the equation

$$k = \frac{\log \frac{E_1 - E_\infty}{E_2 - E_\infty}}{t_2 - t_1}$$

where E_1, E_2 . . . . E_∞ are the measured extinctions and t_1, t_2 the corresponding time in minutes.

pH *Control*

As usual, variations due to primary and secondary salt effects were avoided by using a constant ionic strength, $\mu = 0.110$, in all comparable experiments. In the general case the solvent contained 0.100 molar potassium chloride, 0.0100 *M* buffer salt, and the corresponding uncharged form of the buffer $2 \times 10^{-3} - 1 \times 10^{-2}$ molar.

In those cases where it was necessary to increase the buffer salt, the potassium chloride was decreased correspondingly to maintain $\mu = 0.110$. The contribution of potassium chloride to the total ionic strength was always greater than 75%. Thus the possibility of specific salt effects was reduced, though probably not eliminated.

For the solvent mixture 50/50 w/w methanol–water the activity coefficients of the hydrogen ion and the acidity constants of acids are not well known. However, since μ was held constant, the activity coefficient of the hydrogen ion was constant and the activity was therefore proportional to the concentration. In this way all kinetic constants for $[H^+]$ catalysis have been referred to hydrogen-ion concentrations. The pH measurements were done with a Beckman (1190–80) glass electrode in a cell, with negligible liquid junction potential, of the type

Glass electrode	KCl 0.100 *M* Buffer salt 0.0100 *M* Uncharged buffer 3×10^{-3} *M*	0.100 KCl	AgCl Ag

As a reference point a known solution of perchloric acid (say 0.00600 *N* perchloric acid, corresponding to a pH = 2.222) was made up to $\mu = 0.110$ with potassium chloride in the given solvent. By relating the measured potential of a buffer solution to the potential of the reference solution, μ, solvent, and temperature being identical, the hydrogen-ion concentration was obtained.

From the hydrogen-ion concentration and the ratio $[Ac^-]/[HAc]$ it was possible to derive the value of the acidity constant of acetic acid valid for the given solvent and $\mu = 0.110$ by the usual equation

$$K_c = \frac{[H^+]\,[Ac^-]}{[HAc]}.$$

Table I gives the value of K_c for three temperatures.

RESULTS

In all experiments the rates of hydrolysis of the compounds investigated have been found to be first-order with respect to benzalaniline concentrations. No trends in the first-order constants were observed within the runs (as is

TABLE I

ACIDITY CONSTANTS OF ACETIC ACID IN 50/50 (w/w) METHANOL–WATER. $\mu = 0.110$

$t°$	$K_c \times 10^6$
0° C.	4.28
10° C.	4.59
20° C.	4.68

TABLE I*a*

HYDROLYSIS OF BENZALANILINE IN 50/50 METHANOL–WATER—UNBUFFERED
$\mu = 0.110$; KCl = 0.0110; a trace of $HClO_4$ added; pH = 6.40; temperature +10.0° C.; $\lambda = 320$ mμ; 13 mgm. benzalaniline added to 230 cc. cell.

t, min.	E	$E-E_\infty$	$\log(E-E_\infty)$	$_4\Delta$	$-_4\Delta t$	k	Δ	$-\Delta t$	k
3.95	1.063	1.015	$\underline{0}.006$				..	....	....
5.42	0.815	0.767	$\bar{1}.885$				0.000	0.00	....
6.07	0.731	0.683	$\bar{1}.834$	0.341	4.30	0.0793	....	....	....
7.60	0.569	0.521	$\bar{1}.717$	0.310	3.96	0.0783	0.168	2.18	(0.0771)
8.25	0.510	0.462	$\bar{1}.665$	0.320	4.06	0.0788	0.220	2.83	0.0777
9.38	0.424	0.376	$\bar{1}.575$	0.331	4.18	0.0792	0.310	3.96	0.0783
10.13	0.375	0.327	$\bar{1}.514$	0.373	4.77	0.0782	0.371	4.71	0.0788
11.78	0.291	0.243	$\bar{1}.386$	0.323	4.12	0.0784	0.499	6.36	0.0785
13.02	0.244	0.196	$\bar{1}.292$	0.353	4.55	0.0776	0.593	7.60	0.0780
13.50	0.227	0.179	$\bar{1}.252$	0.259	3.32	0.0780	0.633	8.08	0.0783
14.68	0.193	0.145	$\bar{1}.161$	0.224	2.90	0.0772	0.724	9.26	0.0782
15.10	0.182	0.134	$\bar{1}.127$	0.222	2.92	(0.0760)	0.758	9.68	0.0783
15.92	0.165	0.117	$\bar{1}.068$				0.817	10.50	0.0778
16.42	0.155	0.107	$\bar{1}.030$				0.855	11.00	0.0777
60′	0.048					0.0783			0.0782

$H^+ = 3.55 \times 10^{-7}$
$k_{H^+} = 1.97 \times 10^{+8}$ (±5%)

TABLE I*b*

HYDROLYSIS OF BENZALANILINE IN 50/50 w/w METHANOL–WATER WITH PHOSPHATE BUFFER
Temperature +10.0° C.; $\mu = 0.110$; KCl = 0.105; $KHPO_4 = 0.00125M$;
$KH_2PO_4 = 0.00125M$; $\lambda = 350$ mμ; pH = 7.63

t, min.	$E-E_\infty$	$\log(E-E_\infty)$	Δ	$-\Delta t$	$\Delta x/\Delta t \times 10^3$	Δ	$-\Delta t$	$k \times 10^3$
1.52	1.354	0.132						
3.68	1.313	0.118				0.000	0.00	—
7.03	1.245	0.096	0.120	16.41	7.32	—	—	—
11.90	1.139	0.057	0.153	20.12	7.61	0.061	8.22	7.42
17.93	1.029	$\underline{0}.012$	0.161	20.87	7.71	0.106	14.25	7.45
23.80	0.922	$\bar{1}.965$	0.164	21.37	7.68	—	—	—
27.90	0.861	$\bar{1}.935$	0.157	20.10	7.81	0.183	24.22	7.56
33.27	0.781	$\bar{1}.893$	0.171	22.47	7.60	0.225	29.59	7.60
38.03	0.716	$\bar{1}.855$	0.179	23.25	7.70	0.263	34.35	7.66
46.27	0.622	$\bar{1}.794$	0.173	22.86	7.57	0.324	42.59	7.60
51.15	0.570	$\bar{1}.756$	0.175	23.40	7.48	0.362	47.47	7.62
56.73	0.524	$\bar{1}.720$	0.168	21.88	7.68	0.398	52.45	7.60
61.43	0.479	$\bar{1}.680$	0.174	22.77	7.65	0.438	57.75	7.58
68.15	0.423	$\bar{1}.626$	—	—	—	0.492	64.47	7.64
73.92	0.382	$\bar{1}.582$	—	—		0.536	70.24	7.64
					$k_{av} = 7.62 \times 10^{-3}$			$k_{av} = 7.61 \times 10^{-3}$

TABLE Ic

HYDROLYSIS OF BENZALANILINE IN 50/50 w/w METHANOL–WATER AT 10.0° C.
$\mu = 0.110$; KCl = 0.1000 M; NaAc = 0.0100 M; HAc = 0.002297;
$\lambda = 320$ mμ; $I_0 = 50\mu$Å; 13 mgm. of benzalaniline used.

t' / $t = t' - 4''$	I	E	$E-E_\infty$	log $E-E_\infty$	Δ	$-\Delta t$	k	Δ	$-\Delta t$	k
1′ 45″	42	1.076	0.961	$\bar{1}$.983						
2′ 00″	57	0.943	0.828	$\bar{1}$.918						
2′ 15″	74	0.830	0.715	$\bar{1}$.854				0.00	0.00	
2′ 30″	90	0.745	0.630	$\bar{1}$.799				—	—	
2′ 45″	106	0.674	0.559	$\bar{1}$.747	$\bar{1}$.236	1.00	0.236	0.197	0.50	(0.214)
3′ 45″	185	0.432	0.317	$\bar{1}$.501	0.482	2.00	(0.241)	0.353	1.50	0.235
4′ 00″	200	0.398	0.283	$\bar{1}$.452	0.466	2.00	0.233	0.402	1.75	0.230
4′ 15″	217	0.362	0.247	$\bar{1}$.393	0.461	2.00	0.231	0.561	2.00	0.231
4′ 30″	233	0.332	0.217	$\bar{1}$.337	0.462	2.00	0.231	0.517	2.25	0.230
5′ 45″	300	0.222	0.107	$\bar{1}$.030	0.471	2.00	0.236	0.824	3.50	0.235
6′ 00″	308	0.210	0.095	$\bar{2}$.978	0.474	2.00	0.237	0.876	3.75	0.234
6′ 15″	315	0.200	0.085	$\bar{2}$.930	0.463	2.00	0.231	0.924	4.00	0.231
6′ 30″	321	0.192	0.077	$\bar{2}$.886	0.451	2.00	(0.225)	0.968	4.25	(0.228)
							k_{av} = 0.234			k_{av} = 0.232

Note: Av. % deviation from the mean = about 1%.

evident from the data of three typical runs given in Table I*a*, I*b*, and I*c*) and these were normally followed to 85% completion. The hydrolysis proceeds to at least 98% based on the disappearance of the benzalaniline. The average values of the over-all rate constants were reproducible to 1%. Deviations of points within any one run were random and seldom exceeded 3%. Under our experimental conditions, the pH readings could be made to 0.01 pH unit and this error was consequently added to those in the over-all rate when calculating k_{H^+}.

It is clear that the rate is strongly dependent on the hydrogen ion concentration although these data do not show complete linearity. The addition of sodium hydroxide, 10^{-3} molar, gave a value of $k < 10^{-4}$ at room temperature, indicating that base catalysis and water catalysis are negligible.

Further investigation in acetate buffers showed that, where the pH was kept constant the rate varied with the amount of buffer (μ remaining constant). These data have been summarized in Fig. 3. It can be seen that the slopes of the curves are determined by the increase of [HAc] and not that of [Ac^-]. This leads to the general rate equation

$$k = a[\mathrm{HAc}] + b([\mathrm{H^+}] = \text{const.}) \qquad [1]$$

TABLE II

RATE CONSTANTS FOR THE HYDROLYSIS OF BENZALANILINE IN DIFFERENT BUFFERS AT +10.0° C., $\mu = 0.110$.
SOLVENT METHANOL–WATER 50/50 w/w

Buffer	pH	k, min.$^{-1}$	$k/[\mathrm{H^+}]$ min.$^{-1}$
Acetate	5.68	$4.49 \cdot 10^{-1}$	$2.16 \cdot 10^{+5}$
Phosphate	7.6	$7.28 \cdot 10^{-3}$	$2.9 \cdot 10^{+5}$
Veronal	8.7	$6.36 \cdot 10^{-4}$	$3.2 \cdot 10^{+5}$

where b is proportional to the $[H^+]$ as can be seen from Table III. Thus it is evident that the rate equation has the form of special and general acid catalysis

$$k = k_{H^+}[H^+] + k_{HAc}[HAc]. \qquad [2]$$

However, at buffer concentrations lower than 10^{-2} M in NaAc, deviations from linearity are found in the plot of k versus [HAc] at constant pH(Fig.4). This indicates that Equation 2 is no longer valid.

TABLE III

PARAMETERS FOR EQUATION [1] FOR DIFFERENT ACETATE BUFFERS

Curve	$[H^+]$	a	b	$b/[H^+]$
1	$2.072 \cdot 10^{-6}$	20.0	0.357	$1.72 \cdot 10^{+5}$
2	$1.20 \cdot 10^{-6}$	21.6	0.200	$1.67 \cdot 10^{+5}$
3	$1.055 \cdot 10^{-6}$	19.3	0.187	$1.77 \cdot 10^{+5}$

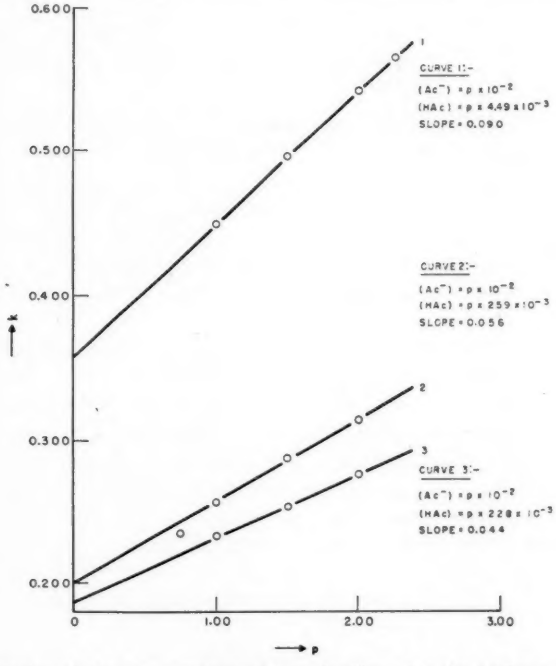


FIG. 3. Variation of the rate constant of benzalaniline with the buffer concentration at +10.0° C.

At −0.1° C. the dependence of k on [HAc] departs from linearity up to 2.50×10^{-2} M NaAc, but the curvature is very small as can be seen from the graph (Fig. 4).

For the data at 20° C. the linear region lies between 7.5×10^{-3} and 1.5×10^{-2} M NaAc.

The experimental data for the rate of hydrolysis in various acetate buffers for the substituted benzalanilines are given in Table IV.

An explanation for the deviations from Equation 2 has not yet been found. However, since there is always a region of linearity at sufficiently high buffer concentrations (except for the small deviations already noted at $-0.1°$ C.), values of k'_{H^+} and k'_{HAc} could be calculated in every case by omitting the points obtained at low buffer concentrations. At the lowest temperature ($-0.1°$ C.) the values of k at $[Ac^-] = 1.50 \times 10^{-2}$; 2.00×10^{-2}; and 2.50×10^{-2} M had been used to obtain approximate values for k'_{H^+} and k'_{HAc}. The analysis of the experimental data in terms of k'_{H^+} and k'_{HAc} obviously involves an approximation and although k'_{H^+} and k'_{HAc} may not be equivalent

TABLE IV

FIRST ORDER RATE CONSTANTS FOR THE HYDROLYSIS OF BENZALANILINES IN ACETATE BUFFERS FOR THE IONIC STRENGTH $\mu = 0.110$

Substance	C_{KCl}	C_{NaAc}	C_{HAc}	k
−0.1° C.				
Benzalaniline	0.1025	0.00750	1.90×10^{-3}	0.136
	0.1000	0.0100	2.53×10^{-3}	0.147
	0.0950	0.0150	3.80×10^{-3}	0.164
	0.0900	0.0200	5.06×10^{-3}	0.177
	0.0850	0.0250	6.32×10^{-3}	0.189
Benzal-*p*-toluidine	0.1000	0.0100	2.53×10^{-3}	0.1190
	0.0950	0.0150	3.80×10^{-3}	0.1276
	0.0900	0.0200	5.06×10^{-3}	0.1378
	0.0850	0.0250	6.32×10^{-3}	0.1465
p-Methoxybenzalaniline	0.1000	0.0100	2.53×10^{-3}	8.78×10^{-2}
	0.0950	0.0150	3.80×10^{-3}	9.83×10^{-2}
	0.0900	0.0200	5.06×10^{-3}	10.49×10^{-2}
	0.0850	0.0250	6.32×10^{-3}	11.06×10^{-2}
Benzal-*p*-anisidine	0.1000	0.0100	2.53×10^{-3}	8.91×10^{-2}
	0.0950	0.0150	3.80×10^{-3}	9.53×10^{-2}
	0.0900	0.0200	5.06×10^{-3}	10.11×10^{-2}
	0.0850	0.0250	6.32×10^{-3}	10.5×10^{-2}
p-Chlorobenzalaniline	0.1000	0.0100	2.53×10^{-3}	0.144
	0.0950	0.0150	3.80×10^{-3}	0.150
	0.0900	0.0200	5.06×10^{-3}	0.155
	0.0850	0.0250	6.32×10^{-3}	0.159
Benzal-*p*-chloroaniline	0.1000	0.0100	2.53×10^{-3}	0.1518
	0.0950	0.0150	3.80×10^{-3}	0.169
	0.0900	0.0200	5.06×10^{-3}	0.180
	0.0850	0.0250	6.32×10^{-3}	0.188
p-Nitrobenzalaniline	0.1000	0.0100	2.53×10^{-3}	8.04×10^{-2}
	0.0950	0.0150	3.80×10^{-3}	8.40×10^{-2}
	0.0900	0.0200	5.06×10^{-3}	8.63×10^{-2}
	0.0850	0.0250	6.32×10^{-3}	8.82×10^{-2}
Benzal-*p*-dimethylaminoaniline	0.1000	0.0100	2.53×10^{-3}	5.10×10^{-2}
	0.0950	0.0150	3.80×10^{-3}	5.28×10^{-2}
	0.0900	0.0200	5.06×10^{-3}	5.52×10^{-2}

TABLE IV (continued)

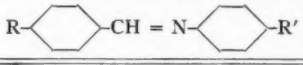
Substance	C_{KCl}	C_{NaAc}	C_{HAc}	k
10.0° C.				
Benzalaniline	0.1075	0.00250	1.12×10^{-3}	0.254
	0.1050	0.00500	2.24×10^{-3}	0.321
	0.1025	0.00750	3.37×10^{-3}	0.391
	0.1000	0.01000	4.49×10^{-3}	0.443
	0.0950	0.01500	6.74×10^{-3}	0.496
	0.0900	0.02000	8.98×10^{-3}	0.540
	0.0875	0.02250	10.10×10^{-3}	0.565
	0.1025	0.00750	1.94×10^{-3}	0.234
	0.1000	0.01000	2.59×10^{-3}	0.255
	0.0950	0.01500	3.89×10^{-3}	0.287
	0.0900	0.02000	5.19×10^{-3}	0.312
	0.1000	0.0100	2.28×10^{-3}	0.232
	0.0950	0.0150	3.42×10^{-3}	0.252
	0.0900	0.0200	4.56×10^{-3}	0.276
Benzal-*p*-toluidine	0.1000	0.0100	2.59×10^{-3}	0.212
	0.0950	0.0150	3.89×10^{-3}	0.229
	0.0900	0.0200	5.19×10^{-3}	0.246
	0.0875	0.0225	5.84×10^{-3}	0.255
	0.1000	0.0100	4.51×10^{-3}	0.358
	0.0950	0.0150	6.77×10^{-3}	0.397
	0.0900	0.0200	9.02×10^{-3}	0.413
p-Methoxybenzalaniline	0.1000	0.0100	5.99×10^{-3}	0.377
	0.0950	0.0150	8.99×10^{-3}	0.404
	0.0900	0.0200	11.98×10^{-3}	0.428
	0.1000	0.0100	4.51×10^{-3}	0.280
	0.0900	0.0200	9.02×10^{-3}	0.325
Benzal-*p*-anisidine	0.1000	0.0100	4.51×10^{-3}	0.201
	0.0950	0.0150	6.77×10^{-3}	0.217
	0.0900	0.0200	9.02×10^{-3}	0.229
	0.1000	0.0100	5.99×10^{-3}	0.268
	0.0950	0.0150	8.99×10^{-3}	0.289
	0.0900	0.0200	11.98×10^{-3}	0.303
p-Chlorobenzalaniline	0.1000	0.0100	4.51×10^{-3}	0.303
	0.0950	0.0150	6.77×10^{-3}	0.318
	0.0900	0.0200	9.02×10^{-3}	0.338
	0.1000	0.0100	5.99×10^{-3}	0.403
	0.0900	0.0200	11.98×10^{-3}	0.449
Benzal-*p*-chloroaniline	0.1000	0.0100	2.59×10^{-3}	0.188
	0.0950	0.0150	3.89×10^{-3}	0.205
	0.0900	0.0200	5.19×10^{-3}	0.219
	0.1000	0.0100	5.99×10^{-3}	0.431
	0.0900	0.0200	11.98×10^{-3}	0.504
p-Nitrobenzalaniline	0.1000	0.0100	4.51×10^{-3}	0.177
	0.0900	0.0200	9.02×10^{-3}	0.186
	0.1000	0.0100	5.99×10^{-3}	0.239
	0.0950	0.0150	8.99×10^{-3}	0.247
	0.0900	0.0200	11.98×10^{-3}	0.251

TABLE IV (concluded)

Substance	C_{KCl}	C_{NaAc}	C_{HAc}	k
20.0° C.				
Benzalaniline	0.1025	0.0075	1.82×10^{-3}	0.358
	0.1000	0.0100	2.53×10^{-3}	0.388
	0.0975	0.0125	3.64×10^{-3}	0.416
	0.0950	0.0150	5.06×10^{-3}	0.448
Benzal-*p*-toluidine	0.1025	0.0075	1.82×10^{-3}	0.313
	0.1000	0.0100	2.53×10^{-3}	0.328
	0.0975	0.0125	3.64×10^{-3}	0.339
	0.0950	0.0150	5.06×10^{-3}	0.359
p-Methoxybenzalaniline	0.1025	0.0075	1.82×10^{-3}	0.243
	0.1000	0.0100	2.53×10^{-3}	0.254
	0.0975	0.0125	3.64×10^{-3}	0.265
	0.0950	0.0150	5.06×10^{-3}	0.272
Benzal-*p*-anisidine	0.1025	0.0075	1.82×10^{-3}	0.171
	0.1000	0.0100	2.53×10^{-3}	0.177
	0.0975	0.0125	3.64×10^{-3}	0.188
	0.0950	0.0150	5.06×10^{-3}	0.196
p-Chlorobenzalaniline	0.1025	0.0075	1.82×10^{-3}	0.255
	0.1000	0.0100	2.53×10^{-3}	0.266
	0.0975	0.0125	3.64×10^{-3}	0.282
	0.0950	0.0150	5.06×10^{-3}	0.297
Benzal-*p*-chloroaniline	0.1050	0.0050	$1.26_5 \times 10^{-3}$	0.243
	0.1025	0.0075	1.82×10^{-3}	0.268
	0.1000	0.0100	2.53×10^{-3}	0.291
	0.0975	0.0125	3.64×10^{-3}	0.311
	0.0950	0.0150	5.06×10^{-3}	0.327
p-Nitrobenzalaniline	0.1025	0.0075	1.82×10^{-3}	0.155
	0.1000	0.0100	2.53×10^{-3}	0.158
	0.0975	0.0125	3.64×10^{-3}	0.161
	0.0950	0.0150	5.06×10^{-3}	0.167
Benzal-*p*-dimethylaminoaniline	0.1025	0.0075	1.82×10^{-3}	0.133
	0.1000	0.0100	2.53×10^{-3}	0.138
	0.0975	0.0125	3.64×10^{-3}	0.139
	0.0950	0.0150	5.06×10^{-3}	0.145

TABLE V

RATE CONSTANTS FOR HYDROGEN-ION CATALYSIS AND ACETIC ACID CATALYSIS OF THE HYDROLYSIS OF SUBSTITUTED BENZALANILINES CALCULATED FROM MEASUREMENTS IN ACETATE BUFFERS



R	R′	−0.1° C.		+10.0° C.		+20.0° C.	
		k'_{H^+}	k'_{HAc}	k'_{H^+}	k'_{HAc}	k'_{H^+}	k'_{HAc}
H–	–H	$1.17 . 10^{+5}$	9.9	$1.70 . 10^{+5}$	20.0	$2.29 . 10^{+5}$	45.9
H–	$-CH_3$	$9.28 . 10^{+4}$	7.2	$1.49 . 10^{+5}$	12.8	$2.25 . 10^{+5}$	24.1
CH_3O–	–H	$7.37 . 10^{+4}$	4.9	$1.19 . 10^{+5}$	8.57	$1.81 . 10^{+5}$	15.8
H–	$-OCH_3$	$5.20 . 10^{+4}$	3.0	$8.45 . 10^{+4}$	6.1	$1.23 . 10^{+5}$	13.2
Cl–	–H	$8.87 . 10^{+4}$	2.8	$1.25 . 10^{+5}$	7.78	$1.80 . 10^{+5}$	21.7
H–	–Cl	$9.30 . 10^{+4}$	5.4	$1.30 . 10^{+5}$	12.1	$1.81 . 10^{+5}$	29.6
NO_2–	–H	$5.12 . 10^{+4}$	1.2	$8.20 . 10^{+4}$	2.0	$1.21 . 10^{+5}$	6.3
H–	$-N(CH_3)_2$	$4.32 . 10^{+4}$	1.7			$1.02 . 10^{+5}$	6.3
$^+H(CH_3)_2N$–	–H	3.71	—			15.7	—

to the true catalytic constants for special and general acid catalysis, nevertheless they do provide a basis for comparing the effect of substituents.

The data for k'_{H^+} and k'_{HAc} for three temperatures are given in Table V. It must be emphasized that it may not be permissible to apply these k'_{H^+} values to buffer solutions other than acetate or to unbuffered solutions before the anomalous behavior at low buffer concentrations has been explained.

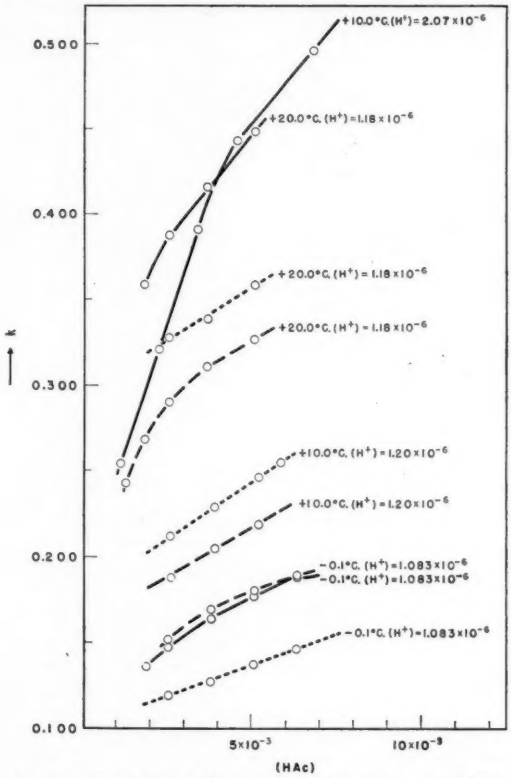


FIG. 4. Deviations from linearity for the general acid catalysis of substituted benzalanilines. Benzalaniline————————, Benzal-*p*-toluidine- - - - - - - , Benzal-*p*-chloroaniline– – – – – – – .

Para-dimethylaminobenzalaniline provides a special case. Whereas the rate constants in acetate buffers are of the same magnitude as the other compounds, the rate in strong acid ($[H^+] = 10^{-3} - 10^{-2}$), in contrast, is still measurable. Fig. 5 shows the dependence of rate on the $[H^+]$ in the region mentioned. This figure leads to the empirical equation

$$-dX/dt = 2.303\, kX = 2.303\, X\, \{k_1[H^+] + k_2\} \qquad [3]$$

in which $k_1 = 15.7$ and $k_2 = 0.337$ for 20° C. There are two possibilities: either

$$X = [B]$$

or

$$X = [BH^+]$$

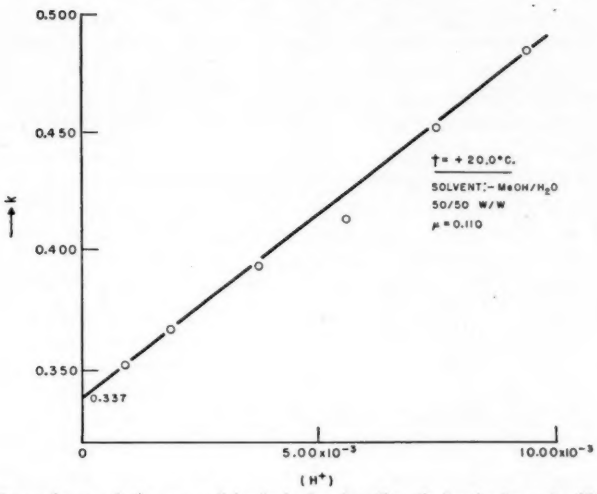


FIG. 5. Dependence of the rate of hydrolysis of *p*-dimethylaminobenzalaniline in strong acids on the hydrogen ion concentration.

where B is the *p*-dimethylaminobenzalaniline and BH^+ the corresponding ammonium ion.

If $X = [B]$, then it is not clear why an uncatalyzed reaction is observed, when at the same time the hydrogen catalyzed reaction is four powers of 10 lower than for the unsubstituted benzalaniline and this in spite of the fact that the *p*-dimethylamino compound in acetate buffer hydrolyzes with a rate comparable to the other benzalanilines. However, if $X = [BH^+]$, where a proton is on the substituted nitrogen, we have to expect that the acid catalyzed hydrolysis of this ion will be slower by a few powers of 10. This follows from the general experience of the influence of this substituent on acidity constants and rate constants (5, 7). Furthermore it is reasonable that dimethylaminobenzalaniline should possess the same order of basicity as the corresponding azobenzene (6) or stilbene (1) compounds which are transformed into cations in the region of pH 4.5.

Equation 3 can now be written

$$-dX/dt = 2.303\, k_1\, [BH^+]\, [H^+] + 2.303\, k_2\, [BH^+]\,. \qquad [4]$$

The second term of [4] does not refer to an uncatalyzed reaction, but rather to the hydrogen ion catalyzed hydrolysis of the free base, which is present in very low concentration. If a substitution is made in terms of the acidity equilibrium for $[BH^+]$

$$[BH^+] = \frac{[B]\,[H^+]}{K}$$

in equation [4], then

$$-\frac{dX}{dt} = 2.303\, k_1\, [BH^+]\, [H^+] + 2.303\, \frac{k_2}{K}\, [B][H^+] \qquad [5]$$

where $k_1 = k_{H^+}^{BH^+}$ and $\frac{k_2}{K} = k_{H^+}^{B}$.

The measured value, k_2, is the product of the rate constant, $k_{H^+}^{B}$, for the hydrogen ion catalyzed reaction of B and the acidity constant, K, of the cation BH^+.

In the case of the compound with the dimethylamino group on the aniline side, the hydrolysis in acid solution, $[H^+] = 10^{-3}$ molar, is too fast to be measured. If some of the substance is added to such a solution there is the development of a red color probably caused by the formation of BH^+ which disappears after a few seconds. The rate in acetate buffer (Table V) is, however, quite normal.

Effect of Substituents

From a comparison of rate data (Table V) it is evident that the effects of para substituents differ from those that normally lead to the Hammett relation. Here the general effect of a substituent is to reduce the rate, whether

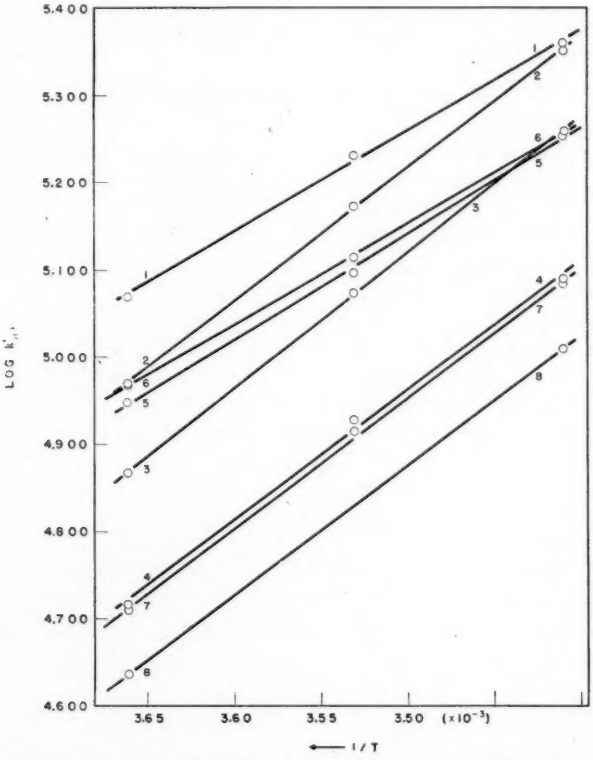


FIG. 6. Temperature dependence of log k'_{H^+}, benzalaniline (1), benzal-*p*-toluidine (2), *p*-methoxybenzalaniline (3), benzal-*p*-anisidine (4), *p*-chlorobenzalaniline (5), benzal-*p*-chloroaniline (6), *p*-nitrobenzalaniline (7), benzal-*p*-dimethylaminoaniline (8).

that substituent would normally be considered to render the nitrogen more or less basic. Even in the case of the Cl and NO_2 substituents where the shift in rate is in the predicted direction, the magnitude of the change is not related to Hammett's σ values. It will be noted that the effect of substituents is larger for the uncharged catalyst, HAc. Further, the relative order of the rate constants is not the same at each temperature.

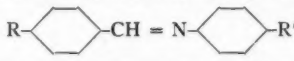
The rate for the charged *p*-dimethylammoniumbenzalaniline is reduced by a factor of 10^4. This very large change is attributed to the electrostatic repulsion of the proton attacking the N of the azomethine bond.

Arrhenius Constants

The temperature dependence of k'_{H+} for the hydrolysis of the series of para substituted benzalanilines is given by the plot of log k'_{H+} versus $1/T$ in Fig. 6. The approximation to linearity is good and may be taken as support for our method of treating the experimental data. In conformity with normal practice, we have calculated the coefficients for the temperature dependence in terms of the two-constant Arrhenius equation, although we are well aware that such a treatment is but approximate and the terminology implies certain unsupported assumptions. These constants with their average error are given in Table VI.

TABLE VI

ACTIVATION ENERGIES AND LOG *PZ*-VALUES FOR THE ACID CATALYZED HYDROLYSIS OF BENZALANILINES



R	R′	*E*, kcal.	log *PZ*
a. Hydrogen ion catalysis			
H	H	5.3 ± 0.25	9.32 [min.$^{-1}$]
H	CH_3	7.0 ± 0.15	10.57 "
CH_3O	H	7.1 ± 0.15	10.58 "
H	OCH_3	6.8 ± 0.50	10.17 "
Cl	H	5.6 ± 0.40	9.44 "
H	Cl	5.3 ± 0.18	9.20 "
NO_2	H	6.8 ± 0.34	10.17 "
H	$N(CH_3)_2$	6.8 ± .30	10.08 "
$^+H(CH_3)_2N$	H	11.4 ± .25	9.70 "
b. Acetic acid catalysis			
H	H	13.0 ± .75	11.36 [min.$^{-1}$]
H	CH_3	9.9 ± 0.35	8.76 "
CH_3O	H	9.8 ± 0.5	8.51 "
H	OCH_3	12.3 ± 0.6	10.26 "
Cl	H	16.6 ± 0.6	13.72 "
H	Cl	14.2 ± 0.6	12.05 "
NO_2	H	(13.3 ± 0.8)	(10.71) "
H	$N(CH_3)_2$	(12.0 ± 0.8)	(9.88) "

It is evident that the effect of a substituent is to change both E_A and PZ. For the hydrogen-ion catalyzed reaction the unsubstituted compound has the lowest value of E_A but the variations resulting from substitution are less than 2 kcal. For the protonated dimethylaminobenzalaniline the activation energy is 6.1 kcal. higher, but the PZ term changes very little. This result is just the one we would expect on the basis of the electrostatic explanation already proposed.

For the acetic acid catalyzed reaction it is noted that the activation energy for the unsubstituted compound is among the highest, in contrast to the previous series, and the two chlorine substituted compounds are even higher.

As has been found for many other series there is a roughly linear relation between log PZ and E_A for both the proton catalyzed and acetic acid catalyzed reaction, Fig. 7. The slope of these curves is approximately 1.3.

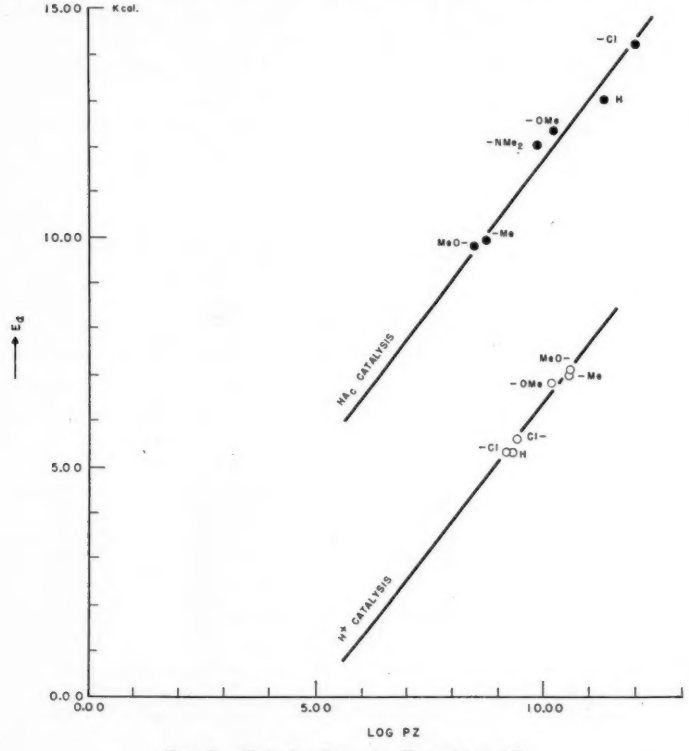


FIG. 7. Relation between E_a and log PZ.

Rate Constants in Unbuffered Solutions

The constancy of k'_{H+} for benzalaniline at +10.0° C. already shown by the data in Table III could be tested in the buffer region of acetic acid between $[H^+] = 2 \times 10^{-6}$ and $[H^+] = 1 \times 10^{-6}$. However, in order to extend the

measurements beyond this pH region and to avoid the uncertainties connected with the deviations from Equation 2 in acetate buffers, it was preferable to carry out rate measurements in very dilute "strong" acids or "strong" bases.

The pH values of these unbuffered solutions have been measured by the aid of a glass electrode and a silver chloride half-cell, with a negligible liquid junction potential, introduced directly into the kinetic cell. Before each kinetic run the glass electrode and the AgCl half-cell were calibrated in a separate thermostated cell containing perchloric acid or acetate buffer of a known pH value.

The results for rate constants of benzalaniline, benzal-*p*-chloroaniline, and *p*-dimethylaminobenzalaniline in unbuffered solutions are given in Table VII

TABLE VII

HYDROLYSIS OF BENZALANILINES IN UNBUFFERED SOLUTIONS OF 50/50 W/W METHANOL–WATER WITH 0.110 *N* KCl AT 10.0° C.

pH	k	log k	$k/[H^+]$
Benzalaniline			
5.65_5	0.135	$\bar{1}.130$	$6.08 \times 10^{+4}$
6.00	0.101	$\bar{1}.004$	$1.01 \times 10^{+5}$
6.78	0.0362	$\bar{2}.559$	$2.18 \times 10^{+5}$
(8.06)	(0.0025)	$\bar{3}.398$	$2.88 \times 10^{+5}$
(8.24)	(0.0016)	$\bar{3}.204$	$2.78 \times 10^{+5}$
9.28	0.00030	$\bar{4}.477$	$5.72 \times 10^{+5}$
10.23	0.000116	$\bar{4}.064$	$1.97 \times 10^{+6}$
(The data in brackets are taken from measurements in which the pH was changing during the course of the run.)			
Benzal-p-chloroaniline			
5.57	0.0875	$\bar{2}.942$	$3.25 \times 10^{+4}$
5.98	0.0537	$\bar{2}.730$	$5.11 \times 10^{+4}$
7.89	0.0025	$\bar{3}.398$	$1.94 \times 10^{+5}$
9.96	7.70×10^{-5}	$\bar{5}.886$	$7.00 \times 10^{+5}$
p-Dimethylaminobenzalaniline			
6.39	0.44	$\bar{1}.644$	$1.08 \times 10^{+6}$
6.49	0.38	$\bar{1}.580$	$1.17 \times 10^{+6}$
10.52	3.93×10^{-4}	$\bar{4}.594$	$1.30 \times 10^{+7}$

and Fig. 8. For each substance it is evident that the rate constant divided by the hydrogen-ion concentration does not give a constant and the equation

$$k = k_{H^+}[H^+]$$

cannot be valid. The plots of log k versus pH in Fig. 8 indicate that the dependence of the rate of the hydrogen-ion concentration is more complicated and further measurements will be necessary before an empirical equation for k as a function of $[H^+]$ can be given.

In this investigation there are two effects which cannot be completely

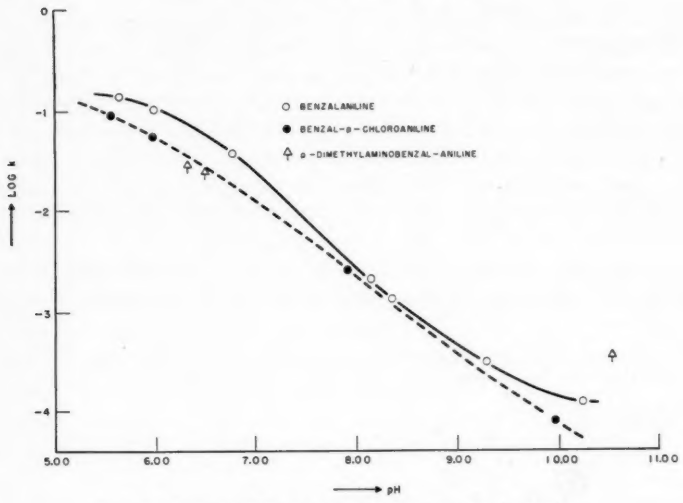


FIG. 8. Benzalaniline–hydrolysis in unbuffered solutions.

understood from the point of view of Brönsted's theory of special and general acid catalysis alone:

(*a*) In buffer mixtures of low buffer concentrations the experimental rates are lower than the values computed from Equation 2.

(*b*) In unbuffered solutions the equation $k = k_{H^+}[H^+]$ is not valid. Both effects have also been found by C. V. King and E. D. Bolinger (3) for the acid catalyzed hydrolysis of diazoacetate ion in aqueous solution and an effect similar to (*a*) was observed by Brönsted, Nicholson, and Delbanco (2) for the decomposition of nitramide in *m*-cresol catalyzed by negatively charged bases.

Before it is possible to reach a fuller understanding of acid catalysis in the hydrolysis of the benzalanilines and to give a more satisfactory treatment of the experimental work reported in this paper, it will be necessary to find the cause of these deviations.

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THE PHOTOLYSIS OF AZOISOPROPANE[1]

By R. W. Durham[2] and E. W. R. Steacie

ABSTRACT

Azoisopropane has been photolyzed by 3660 Å radiation over the temperature range 30–120° C. The effect of pressure indicates an excited molecule mechanism. Excited molecules which decompose give nitrogen and isopropyl radicals; the latter either combine, disproportionate, or react with azoisopropane. The activation energy difference between the two reactions

$$C_3H_7\cdot + C_3H_7.N{:}N.C_3H_7 \rightarrow C_3H_8 + C_3H_6.N{:}N.C_3H_7$$
$$2C_3H_7\cdot \rightarrow C_6H_{14}$$

has been found to be 6.5 ± 0.5 kcal. per mole.

The difference in activation energy between the disproportionation and combination reactions is rendered ambiguous by the possibility of $C_3H_7.N{:}N$ existing at the lower temperatures; but this is certainly small. The ratio of the rates of the two reactions is 0.5 at room temperature.

INTRODUCTION

The photolysis of azoisopropane has not been previously reported in the literature although the thermal decomposition has been studied by Ramsperger (10). This author did not analyze the gaseous reaction products and did not propose any free radical mechanism for the decomposition. It seems reasonable to suppose that the initial reaction in decomposition is to form nitrogen and isopropyl radicals, these radicals then would react with themselves and the remaining azoisopropane.

Weininger and Rice (12) have shown that a molecule of azoethane on absorbing a quantum of radiation is raised to an excited state having a lifetime reasonably long compared to the time between collisions with a normal molecule and hence a proportion of the radiation absorbed by the azoethane is dissipated without reaction. The quantum yield of nitrogen formation is therefore pressure dependent, and although recent work on the photolysis of azomethane (3) has shown that this effect does not occur with the lower homologue it should appear in the photolysis of azoisopropane which has a greater number of internal degrees of freedom.

The object of this research has been therefore to investigate the disproportionation and combination reactions of isopropyl radicals, the rate of reaction of isopropyl with azoisopropane, and to determine whether an excited molecule is produced in the photolysis of azoisopropane.

EXPERIMENTAL

The azoisopropane was prepared after the method of Lochte, Noyes, and Bailey (6). It was purified by vacuum fractionation and stored in a darkened trap attached to the apparatus by means of a mercury cutoff. About 0.2 per cent of C_6H_{14} was always present in the stored azoisopropane which, if allowed to remain, would cause an appreciable error in the C_6H_{14} analysis of runs of low conversion. The procedure used in filling the reaction cell therefore entailed con-

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densing a sample of azoisopropane into the analysis section, removing the residual C_6H_{14}, and then expanding into the filling section of the apparatus. The pressure was measured with a mercury manometer, and the cell then closed off for irradiation. The reaction cell was 10 cm. in length, with a volume of 196 cc., and was almost completely filled by the light beam.

The analysis section consisted of a modified Ward still as described by LeRoy (5), a Toepler pump, and McLeod gauge. A trap ahead of the Ward still maintained at − 75°C. removed the bulk of the unchanged azoisopropane.

The mercury vapor lamp used was the Hanovia 100 watt Alpine burner, its beam collimated with two lenses and two stops. The absorption maximum for azoisopropane is at 3600 Å so that the 3660 Å mercury line was used for the photolysis and was isolated by using two Corning 5860 filters. A selenium photocell connected directly to a sensitive microammeter was placed at the back of the reaction cell to measure the transmitted intensity.

The aluminum block furnace had quartz windows at each end to cut down cooling by convection and the temperature varied only by about 1°C. during a 12 hr. run. The voltage at the furnace and lamp was maintained constant by using a Sorenson voltage stabilizer.

Results

The absorption coefficient of azoisopropane for 3660 Å radiation was found to increase appreciably with temperature. Curves of pressure against log transmission were therefore determined for the temperature at which arbitrary quantum yields were measured. In this way the absorption occurring during a run was known by measuring the pressure of azoisopropane in the cell.

The analytical procedure following a run was as follows.

Most of the unreacted azoisopropane and condensable products was condensed in a side tube with liquid nitrogen before the cell was opened to the analytical section. The remaining condensables were removed by leaving the cell open to the Ward still, cooled with liquid nitrogen for two to three hours, and then the residual nitrogen was pumped into the gas burette. Mass spectrometer analysis of a sample of this gas confirmed that it was pure nitrogen.

On warming the Ward still to − 135°C. the propane and propylene were brought off together and, after the volume and pressure had been measured, a sample of the mixture was analyzed by absorption of the propylene onto a bead of fused mercuric acetate (9).

By plotting a vapor pressure curve at low temperatures for carefully purified azoisopropane and comparing it with that for 2,3-dimethyl butane, the expected C_6 hydrocarbon produced from the combination of two isopropyl radicals, it appeared that a separation of the two compounds could be obtained at a maximum vapor pressure of about 5×10^{-2} mm. By holding the Ward still at − 85°C. and using the preliminary trap described above, it was possible to separate the C_6H_{14} hydrocarbon and measure its volume and pressure; the spread of the points in Figs. 1 and 2 probably represent the analytical error in the C_6H_{14} estimation. The cracking pattern of this hydrocarbon in the mass spectrometer was used to identify it with an authentic specimen of 2,3-dimethyl butane.

A material balance of $N_2 = \frac{1}{2}(C_3H_8 + C_3H_6) + C_6H_{14}$ was obtained with a standard deviation of $\pm 5\%$ about 100% balance, except for one run where the low pressure made analysis difficult. In three runs it was found that all the C_6H_{14} had not been removed before the runs were started so that the correct amount was calculated by difference from the nitrogen and propane plus propylene analyses. The rate of nitrogen production was found to be directly proportional to the incident intensity of the radiation for a constant azoisopropane concentration.

Discussion

The following reaction scheme is proposed to account for the variation in products with varying radiation intensity, absorption, and concentration of azoisopropane. AP refers to the normal molecule of azoisopropane whilst AP^x is the excited state.

$$C_3H_7.N{:}N.C_3H_7 \xrightarrow{h\nu} AP^x$$

$$AP^x \rightarrow N_2 + 2\ \text{iso-}C_3H_7 \quad [1]$$

$$AP + AP^x \rightarrow 2\ AP \quad [2]$$

$$2\ \text{iso-}C_3H_7 \rightarrow C_3H_6 + C_3H_8 \quad [3]$$

$$\rightarrow C_6H_{14} \quad [4]$$

$$\text{iso-}C_3H_7 + AP \rightarrow C_3H_8 + C_3H_6.N{:}N.C_3H_7 \quad [5]$$

It is seen by inspection of the above scheme that

$$\frac{R_{C_3H_6}}{R_{C_6H_{14}}} = \frac{k_3}{k_4}$$

so that the rate of combination of isopropyl radicals compared with the disproportionation rate can be obtained from the propylene to C_6H_{14} ratio. By assuming a constant steady state concentration of isopropyl the following two equations, analogous to those obtained in the photolysis of diethyl ketone (4), can be applied

$$\frac{R_{C_3}}{R_{C_6H_{14}}} = \frac{2\,k_3}{k_4} + \frac{k_5}{k_4^{\frac{1}{2}}} \cdot \frac{[AP]}{R_{C_6H_{14}}^{\frac{1}{2}}} \quad [7]$$

$$\frac{\Delta R_{C_3}}{R_{C_6H_{14}}} = \frac{k_5}{k_4^{\frac{1}{2}}} \cdot \frac{[AP]}{R_{C_6H_{14}}^{\frac{1}{2}}} \quad [8]$$

R_{C_3} represents the rate of formation of $C_3H_6 + C_3H_8$ and ΔR_{C_3} is $(C_3H_8 - C_3H_6)$. $R_{C_6H_{14}}$ is expressed in molecules/sec./cc. of cell volume and the concentration of azoisopropane in molecules/cc.

The large radical appearing in reaction [5] appears to be relatively stable and probably disappears by dimerization. It does not seem to remove isopropyl radicals to form $C_6H_{13}.N{:}N.C_3H_7$ because a good material balance is obtained. Also it does not appear to react with an isopropyl radical to give C_6H_{14} and C_3H_6. Such a reaction as this would cause $R_{C_6H_{14}}$ to increase with temperature through the $C_3H_6.N{:}N.C_3H_7$ concentration increasing with temperature whereas $R_{C_6H_{14}}$ actually decreases with temperature. Similarly the reaction

$$C_3H_6.N{:}N.C_3H_7 \rightarrow C_3H_6 + N_2 + C_3H_7$$

is not important as C_3H_6 does not increase with temperature.

Table I shows the results obtained by varying concentration of azoisopropane, radiation intensity, and temperature, and they have been used in Figs. 1 and 2

TABLE I

PHOTOLYSIS OF AZOISOPROPANE

[AP] molecules, cc.$^{-1}$ $\times 10^{-18}$	$R_{C_3H_6}/R_{C_6H_{14}}$	$\Delta R_{C_3}/R_{C_6H_{14}}$	$R_{C_3}/R_{C_6H_{14}}$	$R_{C_6H_{14}}$ molecules, cc.$^{-1}$ sec.$^{-1}$ $\times 10^{-12}$	$R_{C_6H_{14}}^{\frac{1}{2}}$ $\times 10^{-6}$	[AP]/$R_{C_6H_{14}}^{\frac{1}{2}}$ molecules$^{\frac{1}{2}}$ cc.$^{-\frac{1}{2}}$ sec.$^{\frac{1}{2}}$ $\times 10^{-12}$	T, °K.	R_{N_2} molecules per sec. per cc. of reaction volume	Incident intensity, arbitrary units
0.55	0.58	0.042	1.20	1.99	1.41	0.390	303	3.26	1.00
0.90	0.55	0.096	1.19	2.82	1.68	0.536		4.87	1.00
1.32	0.51	0.082	1.10	3.56	1.89	0.698		5.02	1.00
0.27	0.53	0.050	1.12	1.23	1.11	0.243		1.86	1.00
0.69	0.57	0.070	1.21	2.20	1.49	0.463		3.49	0.954
0.18	0.53	0.050	1.12	0.86	0.93	0.194		1.254	0.952
1.29	0.53	0.120	1.18	1.03	1.02	1.264		1.57	0.312
0.53	0.57	0.088	1.24	1.42	1.19	0.445		2.38	0.767
1.00	0.54	0.096	1.17	1.97	1.41	0.709		3.13	0.797
0.80	0.56	0.075	1.20	1.67	1.29	0.620		2.65	0.797
0.93	0.55	0.100	1.19	1.88	1.37	0.679		2.93	0.775
1.017	0.48	0.119	1.07	0.753	0.869	1.170		1.21	0.347
0.670	0.56	0.116	1.23	0.521	0.720	0.931		1.02	0.338
1.18	0.29	0.57	1.14	1.92	1.39	0.849	394	2.76	0.513
0.70	0.35	0.51	1.22	1.15	1.07	0.654		1.84	0.496
1.14	0.36	0.86	1.59	1.46	1.21	0.942		2.59	0.500
0.57	0.37	0.53	1.26	1.02	1.01	0.564		1.57	0.516
0.38	0.40	0.47	1.25	0.66	0.81	0.469		1.07	0.485
0.18	0.41	0.17	1.20	0.38	0.62	0.290		0.61	0.490
1.11	0.44	0.38	1.25	1.23	1.11	1.000	354	2.00	0.487
0.79	0.40	0.254	1.05	1.13	1.06	0.745		1.55	0.487
0.44	0.43	0.25	1.10	0.657	0.81	0.544		1.01	0.472
0.22	0.46	0.10	1.03	0.402	0.63	0.350		0.56	0.460
1.53	0.40	0.64	1.42	0.966	0.98	1.560		0.85	0.190
0.88	0.40	0.45	1.25	0.425	0.65	1.350		0.68	0.180
0.11	0.46	0.125	1.06	0.134	0.37	0.300		0.30	0.434
1.24	0.50	0.270	1.27	1.03	1.02	1.220	335	1.75	0.434
0.72	0.50	0.200	1.20	0.834	0.914	0.788		1.34	0.425
1.62	0.47	0.298	1.24	1.16	1.08	1.500		1.90	0.428
1.59	0.48	0.382	1.35	0.684	0.828	1.920		1.20	0.253
0.926	0.49	0.302	1.28	0.527	0.725	1.280	335	0.90	0.246
0.841	0.50	0.222	1.23	0.723	0.850	0.989		1.21	0.372
0.571	0.49	0.206	1.17	0.579	0.760	0.751		0.92	0.363
0.231	0.44	0.170	1.04	0.295	0.544	0.425		0.47	0.350
0.428	0.46	0.227	1.14	0.452	0.673	0.636		0.80	0.310
0.115	0.50	0.129	1.13	0.138	0.372	0.310		0.32	0.338

to obtain $k_5/k_4^{\frac{1}{2}}$ by plotting $\Delta R_{C_3}/R_{C_6H_{14}}$ against $[AP]/R_{C_6H_{14}}$. The logarithms of the least squares values of $k_5/k_4^{\frac{1}{2}}$ have been plotted against the reciprocal temperatures in order to evaluate $E_5 - \frac{1}{2}E_4$; from Fig. 3 this activation energy difference is calculated by the method of least squares to be 6.5 ± 0.5 kcal. per mole and the ratio of the steric factors $P_5/P_4^{\frac{1}{2}}$ is 5×10^{-4}; 6.5 kcal. would be a minimum value for the activation energy involved in the abstraction of a tertiary hydrogen atom from azoisopropane as it is possible that E_4 is not zero. Trotman-Dickenson, Birchard, and Steacie (11) obtained values of 7.6 and 7.8 kcal. for the abstraction of tertiary hydrogen atoms from isobutane and 2,3-dimethyl butane by methyl radicals which are similar reactions to the above. The reaction involving an isopropyl radical would be expected to be slightly higher in energy due to the formation in this reaction of the weaker secondary C–H bond of propane. The ratio of the steric factors in the methyl radical work was also

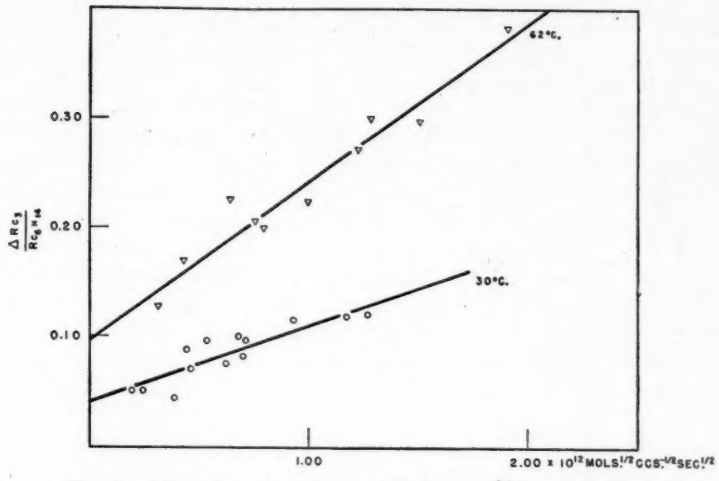

FIG. 1. $\Delta R_{C_3}/R_{C_6H_{14}}$ plotted against $[AP]/R_{C_6H_{14}}^{1/2}$ at 30° and 62°C.

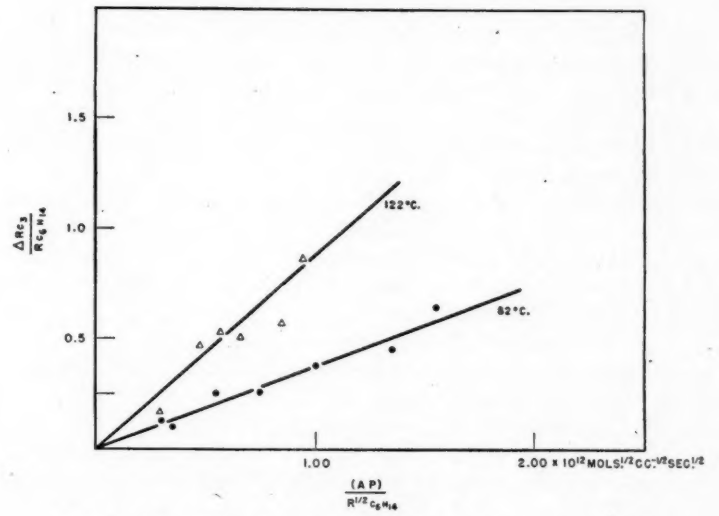

FIG. 2. $\Delta R_{C_3}/R_{C_6H_{14}}$ plotted against $[AP]/R_{C_6H_{14}}^{1/2}$ at 82° and 122°C.

of the order of 10^{-3}. Kutschke, Wijnen, and Steacie (4) obtained an activation energy of 7.5 kcal. for the reaction of an ethyl radical with diethyl ketone, while Ivin and Steacie (2) found 6.2 kcal. for the similar reaction between an ethyl radical and mercury dimethyl. The difference between these reactions and reaction [5] is that a secondary C–H bond is broken compared with a tertiary in azoisopropane, whilst a primary is formed in ethane and a secondary in propane. As the activation energies are in reasonable agreement the primary

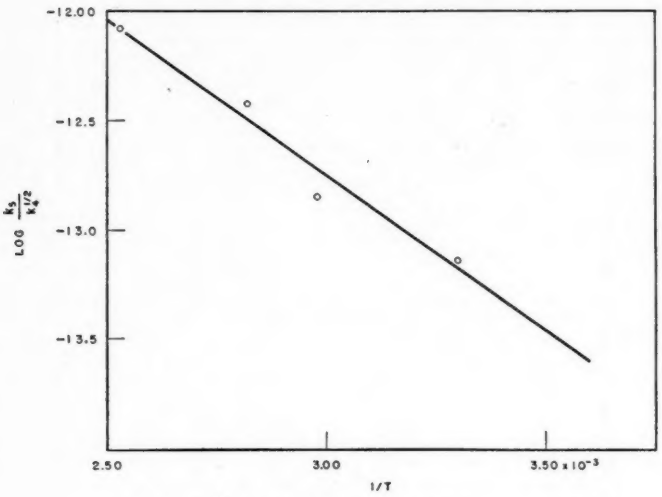

FIG. 3. Arrhenius plot of $k_5/k_4^{\frac{1}{2}}$.

and secondary C–H bond dissociation energy difference must be practically equal to the secondary and tertiary difference in ethane and propane. From a study of the photolysis of di-*n*-propyl ketone, Masson (7) has found the activation energy needed for removal of a secondary hydrogen atom from di-*n*-propyl ketone by the *n*-propyl radical to be 6.5 kcal.; in this case a primary C–H bond is formed in the reaction.

Equation [8] should give a straight line passing through the origin but positive intercepts are obtained on extrapolating the 30°C. and 62°C. graphs to zero value of $[AP]/R_{C_6H_{14}}^{\frac{1}{2}}$. This might be due to the presence of the radical $C_3H_7N{:}N.$ at lower temperatures which would give $C_3H_8 + C_3H_6$ probably more readily than C_6H_{14} by the following reaction.

$$C_3H_7 + C_3H_7.N{:}N. \rightarrow N_2 + C_3H_8 + C_3H_6 \qquad [9]$$

It is also possible that at low pressures the diffusion of radicals to the walls becomes important. Table II shows the variation of k_3/k_4 with increasing temperature. The values in the first column have been obtained by averaging those for a series of runs at each temperature and those in the second column have been calculated from graphs of equation [7] correcting for the intercepts

TABLE II

VARIATION OF RATE CONSTANTS WITH TEMPERATURE

Temperature, °C.	k_3/k_4 average	k_3/k_4 from intercepts
30	0.54	0.51
62	0.48	0.48
81	0.43	0.47
121	0.36	0.38

appearing in Figs. 1 and 2, after the manner of Kutschke, Wijnen, and Steacie (4). It is interesting to note that the value of k_3/k_4 obtained at 30°C. agrees with that of 0.5 obtained by Blacet and Calvert (1) during an investigation of the photolysis of isobutyraldehyde at room temperature. A similar result, namely 0.4 was estimated by Moore and Taylor (8) from the ratio of propane to hexane formation during the mercury photosensitized hydrogenation of propylene at room temperature. The somewhat lower ratio of 0.15 has been obtained in the photolysis of di-*n*-propyl ketone by Masson (7) and is probably related to the different configurations of the normal and isopropyl radicals.

The value of k_3/k_4 appears to fall off with increasing temperature but the effect is relatively small and in view of uncertainty of explanation of intercepts is perhaps not worth discussing in detail. It is, however, possible that the presence of $C_3H_7.N{:}N.$ may be a complication. The activation energy difference between disproportionation and recombination is almost certainly zero and the value of 0.5 for k_3/k_4 a steric effect.

The production of an excited molecule of azoisopropane in the primary step is indicated by the way the rate of nitrogen formation drops off with increasing azoisopropane concentration as is required by reaction [2]. An arbitrary primary process quantum yield ϕ_a has been calculated by dividing the rate of nitrogen production, corrected for variations in incident intensity, by the percentage absorption and making ϕ_a equal to 1 at the extrapolated value of zero azoisopropane concentration. In Fig. 4, ϕ_a has been plotted against concentration for

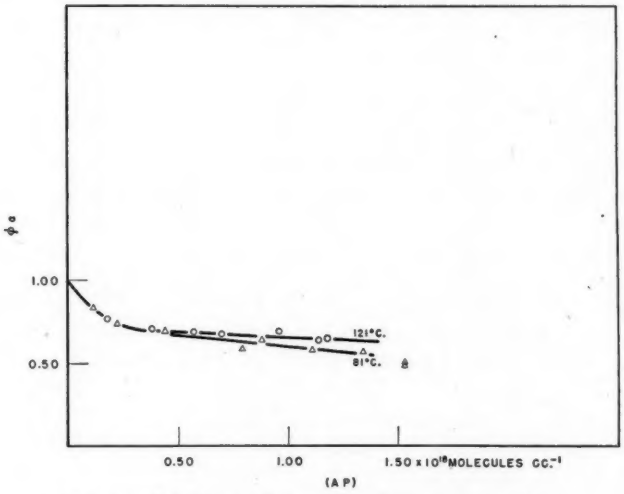

FIG. 4. Plot of ϕ_a against azoisopropane concentration.

two temperatures showing a small increase in quantum yield with temperature at higher azoisopropane concentrations.

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ORGANIC DEUTERIUM COMPOUNDS
V. THE CHLORINATION OF PROPYNE AND PROPYNE-d_4[1]

By L. C. Leitch[2]

ABSTRACT

Chlorination of propyne at 70° C. gave 60 to 65% yields of 1,1,2,2-tetrachloropropane and 15 to 20% yields of *trans*-1,2-dichloro-1-propene. 1,1,2,2-Tetrachloropropane-d_4 was similarly prepared from propyne-d_4. Nearly theoretical yields of *cis*- and *trans*-1,2-dichloro-1-propene were obtained by partial dechlorination of tetrachloropropane. Deuterated *cis*- and *trans*-1,2-dichloro-1-propene were obtained in the same manner from 1,1,2,2-tetrachloropropane-d_4.

INTRODUCTION

Some time ago normal and deuterated *cis*- and *trans*-1,2-dichloro-1-propene were required to establish the configuration of this pair of geometrical isomers. The spectroscopic results of this investigation have already been reported by Bernstein and Powling (1). Since these compounds were prepared from propyne and propyne-d_4 by a novel method, it was felt that the synthetic part of the work should be reported in a separate paper.

cis- and *trans*-1,2-Dichloro-1-propene have been previously prepared from sodium 2,3,3-trichlorobutyrate (7) and 1,2,2-trichloropropane (4) respectively. Neither of these methods is suitable for the preparation of the deuterated dichloropropenes. These compounds might be obtainable, however, from propyne-d_4 (5) by chlorination to 1,1,2,2-tetrachloropropane-d_4 followed by partial dechlorination with zinc dust in ethanol.

Although the literature on the chlorination of acetylene is voluminous (3) the reaction of other acetylenic hydrocarbons with chlorine has not been extensively investigated. Hexyne-1 was reported by Hennion and Welsh (2) to give a 30.6% yield of 1,1,2,2-tetrachlorohexane and a 19.6% yield of *trans*-1,2-dichloro-1-hexene when chlorinated at 40° C. in carbon tetrachloride in the presence of antimony pentachloride. Rengert and Schumacher (6) obtained a mixture of compounds which were not all characterized from the vapor phase chlorination of vinylacetylene at 150° C.

In the present work, the chlorination of propyne was first investigated in carbon tetrachloride at −20, −40, and −60° C. in the presence of antimony pentachloride. The reaction products boiled over a wide range and only low yields of 1,1,2,2-tetrachloropropane were obtained. Chlorination by substitution as well as by addition appeared to have taken place. In the vapor phase, however, propyne reacted smoothly at 65 to 70° C. to give, in 60 to 65% yields, 1,1,2,2-tetrachloropropane. In addition, *trans*-1,2-dichloro-1-propene was obtained in 15 to 20% yields. The *cis*- isomer was prepared by fractional distillation of the mixture resulting from the dechlorination of 1,1,2,2-tetrachloropropane. The corresponding deuterated compounds were prepared from propyne-d_4.

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Contribution from the Division of Applied Chemistry, National Research Council, Ottawa, Canada. Issued as N.R.C. No. 2948.
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EXPERIMENTAL

1,1,2,2-Tetrachloropropane

The apparatus used in these experiments was similar to that described by Taylor and Morey (8). The reactor (2 liters) was heated by means of an infrared lamp at a distance of six inches from the flask. Dry chlorine and propyne were introduced into the reactor through flowmeters in the ratio 2:1. After a short induction period, during which the temperature of the gases in the reactor rose to 60 to 70° C., the reaction started and liquid product began to form. When 17.0 liters of propyne had been introduced at the rate of 2.0 liters per hour, the liquid product was withdrawn, washed with aqueous potassium carbonate, and dried over anhydrous potassium carbonate. The yield was 107 gm.

On distillation at atmospheric pressure in a Stedman column (12 in. × $\frac{3}{4}$ in.) a fraction, b.p. 62 to 98° C., largely at 75° C., was collected. This product was redistilled in a smaller Stedman column (12 in. × $\frac{3}{8}$ in.); it was mainly *trans*-1,2-dichloro-1-propene, b.p. 75° C., n_D^{20} 1.4498. Yield: 15.0 gm. (20%).

The 1,1,2,2-tetrachloropropane was fractionated under reduced pressure. After collecting a forerun (5.5 ml.) up to 79° C. at 64 mm., the main product distilled at 81° C. at 64 mm. The yield of 1,1,2,2-tetrachloropropane, n_D^{20} 1.4866, was 82.5 gm. (63% of the theoretical amount).

Propyne-d_4 prepared as described in a previous paper (5) gave similar yields of 1,1,2,2-tetrachloropropane-d_4, n_D^{20} 1.4848.

cis- and trans-1,2-Dichloro-1-propene

1,1,2,2-Tetrachloropropane (37.5 gm.) was added gradually to a boiling suspension of zinc dust (20.0 gm.) in 200 ml. of ethanol in a 1 liter three-necked round-bottomed flask equipped with a stirrer and reflux condenser. Any allene which was formed owing to the presence of isomeric 1,2,2,3-tetrachloropropane was condensed in a trap cooled to −78° C. by dry ice and acetone. The reaction mixture was heated under reflux for one hour after the chlorocompound had been added. The mixed dichloropropenes formed were then distilled off through a Stedman column as azeotropes with ethanol and water. The yield was nearly quantitative. The product was separated into the *cis*- and *trans*-isomers boiling at 92° and 75° C. respectively by means of a Stedman column. For *trans*-1,2-dichloro-1-propene, n_D^{20} 1.4498; for the *cis* form, n_D^{20} 1.4549.

The corresponding deuterated compounds were prepared in exactly the same way. For *trans*-1,2-dichloro-1-propene, n_D^{20} 1.4479 and for the *cis* form, n_D^{20} 1.4528.

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THE PAPILIONACEOUS ALKALOIDS

XX. *LUPINUS WYETHII* S. WATS. AND *BAPTISIA VERSICOLOR* LODD.[1]

By François Turcotte, Raymond Leduc[2], and Léo Marion

ABSTRACT

An investigation of the basic components of *Lupinus wyethii* S. Wats. has revealed the presence of at least four alkaloids, three of which, i.e., *l*-sparteine, *d*-lupanine, and hydroxylupanine, are known. The fourth has not been found in sufficient quantity to permit proper characterization. A similar investigation of *Baptisia versicolor* Lodd. has yielded three alkaloids, i.e., *d*-sparteine, *l*-lupanine, and *l*-anagyrine.

The first plant under investigation was collected in 1948 through the courtesy of Messrs. S. B. Penick Co., in Paddock No. 1, U.S. Sheep Experiment Station, Dubois, Idaho. It has been identified as *Lupinus wyethii* S. Wats., and voucher specimens are kept under No. 539 (Lichtenfelder) in the Herbarium of the State College of Washington, Pullman, Wash. The plant has been found to contain three well known alkaloids together with a small quantity of a base which could not be identified and was obtained in too scanty a quantity to make its proper characterization possible. The most abundant alkaloid present was *l*-sparteine, while the next in importance was *d*-lupanine. The third, hydroxylupanine, was present in small quantity only. This is the fourth reported occurrence of hydroxylupanine which was first found in *L. polyphyllus* L. (2) and later in *L. angustifolius* L. (1). Octalupine isolated from *L. sericeus* var. *flexuosus* C. P. Smith (4) has been shown to be identical with hydroxylupanine (6). The hydroxylupanine now isolated was characterized by direct comparison with an authentic sample kindly supplied by Dr. F. Galinovsky. The infrared absorption spectra of both bases were superimposable.

The second plant investigated, *Baptisia versicolor* Lodd., was grown at the Dominion Experimental Farm, Ottawa. It was found to contain at least three alkaloids, i.e., *d*-sparteine, *l*-lupanine, and *l*-anagyrine. It has been stated that *B. versicolor* is identical with *B. australis* (5). However, the main alkaloids contained in the latter were *d*-sparteine, cytisine, and N-methylcytisine (7) and therefore the earlier distinction of *B. versicolor* as an individual species was probably justified.

EXPERIMENTAL[3]

A. *Lupinus wyethii*

The dried and ground plant material (whole plant) weighed 8560 gm. It was extracted with methanol in Soxhlet extractors, and the combined methanolic liquor concentrated on the steam bath until most of the solvent had been

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Contribution from the Division of Pure Chemistry, National Research Council, Ottawa, Canada, and the Department of Chemistry, University of Montreal, Montreal, Que. Issued as N.R.C. No. 2949.
[2] *At the time holder of Canadian Industries Limited Fellowship at the University of Montreal.*
[3] *All melting points are corrected.*

removed. The residue was worked up as previously described (7).

The basic product thus obtained consisted of a heavy oil which separated into two layers on standing. It was distilled *in vacuo* and yielded the following fractions: (I) b.p. 90–110° at 0.1 mm., colorless mobile oil, wt. 34.7 gm.; (II) b.p. 120–135° at 0.1 mm., viscous oil, wt. 18.9 gm.; (III) b.p. 150–165° at 0.1 mm., pale yellow resin, wt. 3.7 gm.; (IV) undistilled residue.

l-Sparteine

Fraction I was redistilled and the oil boiling at 95–100° at 0.2 mm. collected while the residue was combined with fraction II. A quantity (1.0 gm.) of the distillate in methanol was converted to the picrate which after recrystallization from boiling methanol consisted of yellow needles, m.p. 208° either alone or in admixture with *l*-sparteine dipicrate. Calcd. for $C_{15}H_{26}N_2.2C_6H_3O_7N_3$: C, 46.80; H, 4.62. Found: C, 46.87, 47.03; H, 4.58, 4.76%.

The bulk of the distillate was dissolved in methanol and to the solution 70% perchloric acid was added dropwise to a phenolphthalein end point. The perchlorate which crystallized was filtered and recrystallized from methanol–ether from which it separated as colorless prismatic needles, m.p. 173° either alone or in admixture with an authentic sample of *l*-sparteine monoperchlorate. Calcd. for $C_{15}H_{26}N_2.HClO_4$: C, 53.83; H, 8.07; N, 8.30. Found: C, 53.60, 53.79; H, 7.99, 7.93; N, 8.09, 8.28%.

d-Lupanine

Fraction II was dissolved in methanol and the solution made acid to Congo red by the dropwise addition of 70% perchloric acid. A crystalline perchlorate separated which after repeated recrystallization from methanol melted at 211° either alone or in admixture with an authentic sample of *d*-lupanine perchlorate. A small quantity of the perchlorate was decomposed and the liberated base redistilled, b.p. 110–115° at 0.1 mm. The free base consisted of a colorless oil, $[\alpha]_D^{23} + 61.1°$ (*c*, 1.145 in acetone). The literature gives $[\alpha]_D + 61.4°$ in acetone for *d*-lupanine (3).

Hydroxylupanine

Fraction III was dissolved in methanol and the solution made acid to Congo red by the cautious addition of 70% perchloric acid. The solution was combined with the mother liquors of the crystallization of *d*-lupanine perchlorate, concentrated, and allowed to stand. It yielded a further small quantity of *d*-lupanine perchlorate which was filtered. The filtrate was concentrated, diluted with water, and alkalized with ammonium hydroxide. The regenerated bases were extracted with chloroform, the extract evaporated to dryness, and the residue dissolved in anhydrous benzene. The solution was chromatographed on activated alumina and the adsorbed base eluted with benzene–ether (90–10), with ether–methanol (99–1), and finally with ether–methanol (95–5). The benzene–ether eluate yielded *d*-lupanine while the two ether–methanol eluates yielded a crystalline base which after recrystallization from acetone consisted of colorless prisms, m.p. 169–170°, either alone or in admixture with an authentic specimen of hydroxylupanine. Calcd. for $C_{15}H_{24}O_2N_2$: C, 68.14;

H, 9.15; N, 10.60. Found: C, 68.46, 68.65; H, 9.27, 9.14; N, 10.73%. The identity of this base with hydroxylupanine was confirmed by comparison of the infrared absorption spectra of both bases which were exactly superimposable.

The undistilled residue (fraction IV) was dissolved in dilute (1:1) hydrochloric acid, the solution filtered through charcoal to remove some insoluble material, alkalized with ammonium hydroxide, and extracted with chloroform. The base recovered from the extract was treated as the original crude base. It yielded further quantities of the same alkaloids.

The final mother liquors which yielded hydroxylupanine were concentrated and made just acid to Congo red with 70% perchloric acid. On concentration and dilution with ether, a very small quantity of a perchlorate crystallized out in long silky needles, m.p. 250–251° (dec.). Found: C, 54.03, 53.99; H, 7.00, 7.17%. Owing to paucity of material it was not possible to purify this salt further nor to characterize it properly.

B. *Baptisia versicolor*

The ground plant (both aerial part and root) (1282 gm.) was extracted with methanol and the extract worked up as described above. The crude base thus obtained (0.995 gm.) was distilled *in vacuo*. It yielded the following fractions: (I) b.p. 65–130° at 0.2 mm., colorless oil, wt. 25 mgm.; (II) b.p. 130–180° at 0.2 mm., yellow oil, wt. 120.5 mgm.; (III) b.p. 180–230° at 0.15 mm., yellow resin, wt. 312 mgm., and an undistilled residue, wt. 538 mgm. Fraction I proved to be untractable. Both fractions II and III were combined and redistilled into the following fractions: (*a*) colorless oil, b.p. 90–120° at 0.15 mm., wt. 39.3 mgm.; (*b*) viscous oil, b.p. 120–140° at 0.15 mm., wt. 96.3 mgm.; (*c*) yellow resin, b.p. 140–180° at 0.15 mm., wt. 95.6 mgm.; (*d*) reddish resin, b.p. 180–230° at 0.15 mm., wt. 26.2 mgm.; (*e*) residue undistilled at 230°, wt. 14.5 mgm.

d-Sparteine

Fraction *a* (39.3 mgm.) was dissolved in methanol and added to a methanolic solution of twice its weight of picric acid. A picrate crystallized as lemon yellow needles, m.p. 207°, and after recrystallization from methanol, m.p. 208°. Calcd. for $C_{15}H_{26}N_2.2C_6H_3O_7N_3$: C, 46.82; H, 4.65; N, 16.18. Found: C, 46.46, 46.67; H, 4.43, 4.38; N, 16.79, 16.59%. Admixture with authentic *d*-sparteine dipicrate failed to alter the melting point whereas admixture with *l*-sparteine dipicrate lowered the melting point to 203°.

The picrate was decomposed by shaking with hydrochloric acid and the recovered base redistilled. It was immediately dissolved in a little methanol and the solution titrated with perchloric acid to a phenolphthalein end point. Addition of ether caused the precipitation of a perchlorate as long colorless needles, m.p. 173°, either alone or in admixture with *d*-sparteine monoperchlorate.

l-Lupanine

Fraction *b* (96.3 mgm.) was dissolved in methanol and the solution made just acid to Congo red by the dropwise addition of 70% perchloric acid. A

perchlorate separated which after recrystallization from methanol–ether melted at 213° and admixture with *l*-lupanine perchlorate failed to depress the melting point. The X-ray powder pattern of this salt and that of *l*-lupanine perchlorate were identical.

l-Anagyrine

Fraction *c* (95.6 mgm.) was converted to perchlorate in methanol in the usual way. The crystalline perchlorate was recrystallized from methanol–ether from which it separated as fine colorless needles, m.p. 310–315° (immersed at 300°) either alone or in admixture with *l*-anagyrine perchlorate. The X-ray powder pattern of the perchlorate and that of anagyrine perchlorate were superimposable.

Fraction *d* and the undistilled residue failed to yield anything tractable.

ACKNOWLEDGMENT

The authors are indebted to Dr. W. H. Barnes and Mrs. H. Sheppard for the X-ray powder patterns and to Dr. R. N. Jones and Mr. R. Lauzon for taking the infrared spectra. One of us (R.L.) expresses his gratitude to Prof. L. Lemay for his help and interest in this problem.

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DETERMINATION OF THE NEUTRON CAPTURE CROSS SECTION FOR THE $Co^{59}(n,\gamma)Co^{60m}$ REACTION[1]

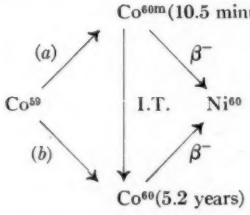
By N. Moss and L. Yaffe[2]

ABSTRACT

A determination of the neutron capture cross section of Co^{59} leading to the excited state of Co^{60} has been made by the activation method. Samples of cobalt were irradiated in the center of the Chalk River nuclear reactor in a pure iron capsule using a pneumatic delivery device. The cobalt activity was counted in a windowless counter and compared with the activity of a strip of pure gold irradiated under identical conditions in the same container. The cobalt and gold were counted with and without cadmium wrapping and the contribution due to epicadmium neutrons allowed for in the calculation. The mean value obtained was 18.3 ± 1.7 barns relative to $\sigma_{Au^{197}} = 93$ barns.

METHOD

Cobalt is monoisotopic of mass 59. On bombardment with slow neutrons the following reactions occur:



The cross section for the reaction leading to the ground state which included the contribution from the Co^{60m} by isomeric transition has been measured by Yaffe, Hawkings, Merritt, and Craven (8) using the activation method. They obtained a value of 34.2 barns which was confirmed soon after by Pomerance (5) using the pile oscillation technique.

It was considered of some interest to determine the cross section for reaction (*a*) leading directly to the excited state. A value of 0.66 barns had previously been obtained by Seren, Friedlander, and Turkel (6). They measured the ratio of β-rays formed by direct transition to Ni^{60} to the soft electrons produced from the γ-rays of the isomeric transition to the Co^{60} ground state. The cross section they obtained was based on this β,γ branching ratio of 10.8/89.2 assuming that each particle, hard or soft, represented a disintegration.

More recently, a much lower value for this ratio has been obtained by Deutsch and Scharf-Goldhaber (2). Using an anthracene scintillation spectrometer to study the decay scheme of Co^{60m}, they found, as in Fig. 1, that only a small fraction (0.28 ± 0.06%) of the disintegrations went directly to Ni^{60}. The greater proportion (i.e., 99%) decays by isomeric transition to the ground state. An almost insignificant amount ($<10^{-4}$%) decays by β emission directly to the stable

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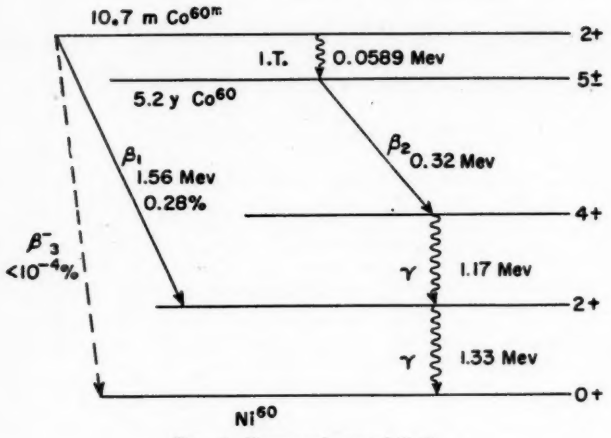

FIG. 1. Decay scheme of Co^{60}.

Ni^{60}. From the observed intensities of the hard γ radiation of the ground state and metastable state activities of Co^{60} they were able to compute the ratio of the neutron capture cross sections for the production of these two states. They found

$$\frac{b}{a} = 1.4 \pm 0.6$$

where a and b represent reactions leading to the excited state and ground state respectively. The value found by Yaffe *et al.* (8) of 34.2 barns includes the contribution for the formation of the Co^{60m} activity, and hence we can write

$$\sigma_b + 99.72\%\ \sigma_a = 34.2 \text{ barns.}$$

Therefore it follows that a value of

$$\sigma_a = 14.2 \begin{matrix} + 4.8 \\ - 2.8 \end{matrix} \text{ barns}$$

should be expected rather than the much lower value of 0.66 barns reported by Seren *et al.* (6).

After a given nuclide is bombarded with neutrons for a time T, the disintegration rate at any time t can be shown to be

$$\frac{dN}{dt} = N(\rho v)\sigma(1 - e^{-\lambda T})e^{-\lambda t}$$

where N = number of atoms of nuclide present
λ = disintegration constant of active product
σ = cross section of nuclide under bombardment
T = time of irradiation
t = time elapsed after irradiation
ρv = neutron flux

If two nuclides A and B are irradiated at the same time under identical conditions, we get

$$\frac{dN_A}{dt} = N_A(\rho v)\sigma_A(1 - e^{-\lambda_A T})e^{-\lambda_A t}$$

and $$\frac{dN_B}{dt} = N_B(\rho v)\sigma_B(1 - e^{-\lambda_B T})e^{-\lambda_B t}.$$

Hence, $$\sigma_A = \frac{dN_A/dt}{dN_B/dt} \cdot \frac{N_B}{N_A} \cdot \frac{1 - e^{-\lambda_B T}}{1 - e^{-\lambda_A T}} \cdot \frac{e^{-\lambda_B t}}{e^{-\lambda_A t}} \cdot \sigma_B .$$

If the cross section of B is known, it is then possible to determine the cross section of A using the above equation.

EXPERIMENTAL

Small samples (ranging from 0.1 to 10 mgm.) of spectroscopically pure cobalt were irradiated in the center of the Chalk River nuclear reactor (flux $\sim 5 \times 10^{13}$ n./cm.^{2}/sec.) for known periods of time ranging from 10 sec. to 10 min.

Accurately measured aliquots (50 μliters each) were taken from a large volume of known cobalt concentration. The samples were evaporated on a small piece of polythene film, which was carefully folded and encased in a very pure iron capsule in which it was despatched to and from the reactor (some 1200 ft.) by a pneumatic tube. The transit time was of the order of 20 seconds. Electric stop watches activated by magnetic relays accurately recorded times of the beginning and end of irradiation.

Spectroscopically pure gold was used as a monitor and accurately weighed samples of this element were irradiated simultaneously with the cobalt. The cross section for the reaction $Au^{197}(n,\gamma)Au^{198}$ was taken to be 93 barns (4).

Immediately after irradiation the cobalt was dissolved off the polythene with nitric acid, made up to a known volume, and a suitable aliquot placed on an aluminum counting tray. The gold foil was dissolved in aqua regia, boiled to prevent aggregate formation, and made up to 2 ml. in a graduated tube. A known aliquot was taken and further diluted in concentrated nitric acid in order to obtain a suitably sized sample for counting.

The activity of the samples was measured in a windowless methane flow chamber (3) which was connected to an amplifier and scaling unit of 1000. The dead time of the chamber was found to be 11 microseconds and counting rates were corrected for this, the greatest correction being of the order of 3%. The background (~ 0.5 counts per sec.) was subtracted where the correction was relevant.

In order that any residual air from the chamber might be swept out, methane gas was passed above and below the absorber for a full minute before counting. The cobalt activity was measured through a 12.85 mgm. per cm.^{2} aluminum absorber to cut out conversion electrons from the 60 kev. internal transition to the 5.3 year ground state. Corrections were made for this branching ratio (0.28%). Decay curves were obtained with various aluminum absorbers and corrections made for the absorption of the 1.56 Mev. β-ray in the aluminum absorber (12.85 mgm. per cm.^{2}) which was used in the experiment.

The back-scattering contribution was found by removing all backing from the counter and depositing sources on thin plastic film (~ 50 μgm. per cm.^{2} of Zapon). The sources on the films, mounted on aluminum rings, were then counted with and without "saturation" back-scattering (9). The Au^{198} (max. energy 0.96 Mev.) contribution was measured directly. That for the Co^{60m} (max. energy

1.56 Mev.) was found by using P^{32} (max. energy 1.71 Mev.) and interpolating a value for the Co^{60m} contribution assuming a linear variation over the small energy range considered. The difference in the contribution due to back-scattering from the Au^{198} (6.3%) and P^{32} (8.0%) was quite small and the cobalt contribution was estimated as 7.6% with very little error. Self-absorption corrections were not made since the sources were essentially "weightless".

The Au^{198} decay curve gave a half-life of 2.69 days and a graphical extrapolation to the end of the irradiation was made to obtain the counting rate at zero time. A typical curve obtained for the Co^{60m} decay is shown in Fig. 2. It can be seen that about one per cent of the disintegrations at zero time were due to relatively long-lived components presumably due to sodium impurities and the 5.3 year ground state. When these components were subtracted by the standard "peeling-off" technique, a small amount (1%) of a substance of half-life of about one hour was found. When this constituent had been subtracted, the Co^{60m} activity at zero time could be obtained. The half-life found was 10.5 ± 0.2 min. which is in good agreement with recent unpublished data on the half-life of Co^{60m} obtained using a continuous recording electroscope (7). The "zero time" value was obtained by graphical extrapolation.

Two of the samples were irradiated for short periods only (10 sec. and 1 min.) to decrease the abundance of the longer-lived components. The cross-section values obtained were substantially the same showing that no large errors were involved in the graphical interpretation.

To allow for the activity due to epicadmium neutrons, successive irradiations of cobalt and gold were made with and without cadmium wrapping. The contribution due to these epicadmium neutrons was 4.0% in the case of cobalt and 10.6% in the case of gold.

RESULTS

The final results are shown in Table I.

TABLE I

Experiment	Co irradiated as	Irradiation time	$\sigma_a \times 10^{24}$ cm.^{2}
1	Nitrate (0.1 mgm.)	10 min.	17.4
2	Nitrate (0.1 mgm.)	10 min.	19.1
3	Nitrate (0.1 mgm.)	10 min.	19.7
4	Nitrate (0.1 mgm.)	10 min.	20.8
5	Wire (10 mgm.)	10 sec.	15.8
6	Wire (0.2 mgm.)	1 min.	17.2
	Mean $\sigma_a = 18.3 \pm 1.7$		

The mean value obtained for the cross section for neutrons of 2200 meters per sec. velocity was 18.3 ± 1.7 barns. This is in good agreement with the value calculated from the data of Deutsch and Scharf-Goldhaber (2). The error quoted is the standard deviation. No attempt has been made to assess systematic errors inherent in the method, since these are assumed to be quite small.

The cross sections leading to the formation of the two cobalt isomers are approximately equal. This confirms a recent observation by Coryell (1) that where an isomeric pair is formed by neutron capture in a target nucleus of spin value

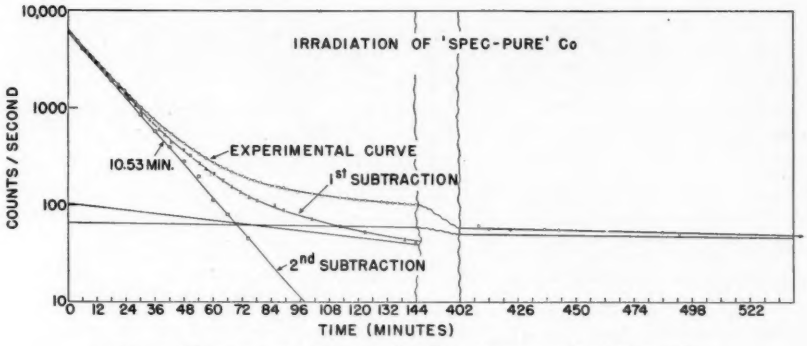

FIG. 2. Decay curve of neutron-irradiated 'spec-pure' cobalt metal.

about midway between the spin values of the two product isomers, then both isomers are formed in about equal amounts. The spin of Co^{59} is 7/2, the two isomers are 2 and 5.

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BIOCHEMISTRY OF THE USTILAGINALES

VIII. THE STRUCTURES AND CONFIGURATIONS OF THE USTILIC ACIDS[1]

By R. U. Lemieux

ABSTRACT

Methanolysis of ustilagic acid and hydrolysis of the methyl esters formed yielded a crystalline acidic fraction which was essentially a mixture of two substances termed the ustilic acids A and B. The acids were separated as their isopropylidene derivatives. The ustilic acids cocrystallize to mixtures with melting points intermediate between those of the pure compounds. Conversion of ustilic acid A, m.p. 112–113° C., $[\alpha]_D$ −8° in methanol, which made up about 70% of the mixture, by hydrogenolysis to palmitic acid, by oxidation with chromic oxide to pentadecanedioic acid, and by lead tetraacetate oxidation followed by hydrogenation to 15-hydroxypentadecanoic acid showed the substance to be an optically active form of 15,16-dihydroxyhexadecanoic acid. Conversion of ustilic acid B, m.p. 140–141° C., $[\alpha]_D$ −10° in methanol, by sodium bismuthate oxidation followed by hydrogenation to 1,14-dihydroxytetradecane, by chromic acid oxidation of its methyl ester followed by hydrolysis of the product, and peroxide oxidation of the α-keto acid thus formed to tetradecanedioic acid, and by hydrogenolysis of the C2-carbon atom through a series of reactions to ustilic acid A, showed the substance to be an optically active form of 2,15,16-trihydroxyhexadecanoic acid. Optically active forms of 2,15-dihydroxypentadecanoic and 2-hydroxypentadecanoic acids were prepared from ustilic acid B. Application of certain empirical rules of rotation to derivatives of these 2-hydroxyacids showed them to possess the D-configuration. Reduction of ustilic acid B with lithium aluminum hydride gave *meso*-1,2,15,16-tetrahydroxyhexadecane. Thus, ustilic acid B was the 2D,15D,16-trihydroxyhexadecanoic acid and the ustilic acid A was the 15D,16-dihydroxyhexadecanoic acid. Several derivatives of the above described acids were prepared.

INTRODUCTION

The new antibiotic (8) termed ustilagic acid was shown (15) to be a mixture of closely related, partially acylated D-glucolipides. Alkaline hydrolysis of ustilagic acid yielded an amorphous substance designated glucoustilic acid and removal of the glucose residues in the latter material yielded a crystalline substance termed ustilic acid (15).

Repeated crystallizations of crude methyl ustilate from methanol yielded a substance with the composition expected for the methyl ester of a dihydroxyhexadecanoic acid and hydrolysis of this ester gave a ustilic acid, m.p. 114–115° C. (15). It was later found, however, that if the crude methyl ustilate, obtained on the methanolysis of glucoustilic acid, was not subjected to purification prior to hydrolysis a ustilic acid preparation was obtained which melted at a higher temperature, in the range 120–126° C., than the above dihydroxyhexadecanoic acid. Furthermore, repeated recrystallizations of the crude ustilic acid did not yield the latter substance but instead gave higher melting materials of indeterminate composition. The infrared spectrum of recrystallized ustilic acid mixture (see Fig. 1) was much different to that of the acid with melting point 114–115° C. and it was therefore apparent that crude ustilic acid was a mixture.

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Methanolysis of 17.2 me. of ustilagic acid, neutral equivalent 801 and saponification equivalent 396, which contained 1.01 acetyl, 0.67 3L-hydroxyhexanoyl, 0.27 3L-hydroxyoctanoyl, 0.05 hexanoyl groups, and 1.96 glucose residues per neutral equivalent, and hydrolysis of the methyl ustilate fraction yielded 17.4 me. of crude ustilic acid, m.p. 122–126° C., with neutral equivalent 296. Periodate oxidation of the crude ustilic acid liberated one mole of formaldehyde per neutral equivalent (see Table II) and it was thus apparent that the components of the ustilic acid mixture contained, on the average, one terminal α-glycol group. Only a trace of steam-volatile acidity was formed in terminal methyl group assays and the ustilic acids therefore appeared free of CH_3–C groups.

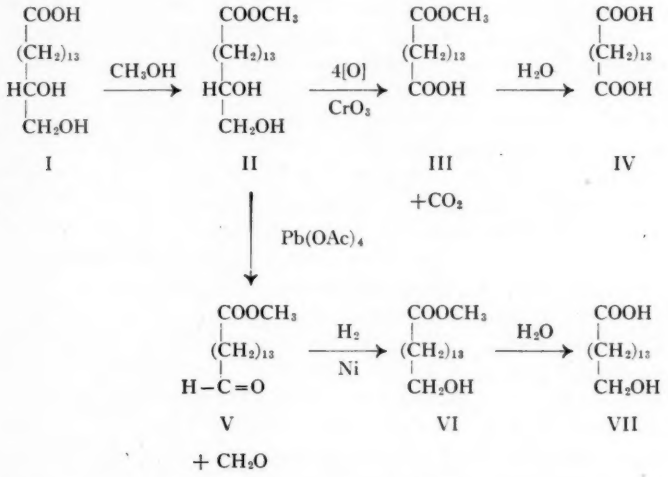
Treatment of the crude ustilic acid mixture with dry acetone containing sulphuric acid yielded a mixture of isopropylidene derivatives. On converting the acid isopropylidene derivatives to methyl ester using diazomethane, it was noticed that considerably less than the calculated amount of diazomethane was required. The esters thus formed were found to possess an isopropylidene group content, 15.3%, which was higher than that which would be expected if the ustilic acids had formed monoisopropylidene derivatives. Furthermore, treatment of the mixture with alkali liberated acetone and it was therefore apparent that the material contained carboxyl groups which were esterified through isopropylidene group linkages. Fractional distillation at about 0.05 mm. pressure separated the mixture of esters, 4.20 gm., into two main fractions; 2.52 gm., b.p. 133–136° C. and 1.16 gm., b.p. 154–156° C. It was thus established that the lower boiling material was a derivative of the major component of the ustilic acid mixture.

Purification of the above described lower boiling fraction by recrystallization from methanol gave a material, m.p. 46–47° C., $[\alpha]_D$ +12° in chloroform, with the composition expected for a methyl isopropylidenedihydroxyhexadecanoate. Methanolysis gave a compound, m.p. 85.5–86° C., $[\alpha]_D$ −7° in methanol, with the composition expected for a methyl dihydroxyhexadecanoate, and hydrolysis of this ester yielded a dihydroxyhexadecanoic acid, m.p. 112–113° C., $[\alpha]_D$ −8° in methanol. This acid is a purer sample of the previously described (15) ustilic acid, m.p. 114–115° C. and is designated ustilic acid A (17). The substance is further characterized by its infrared spectrum (see Fig. 1) and its hydrazide derivative, m.p. 140.5–141.5° C.

Purification of the above described higher boiling fraction by recrystallization from methanol gave a material, m.p. 42.5–43° C., $[\alpha]_D$ +18° in chloroform, with the composition expected for a diisopropylidenetrihydroxyhexadecanoate. Methanolysis of this compound yielded a substance, m.p. 74–75° C., $[\alpha]_D$ −8.5° in methanol, with the composition expected for a methyl trihydroxyhexadecanoate, and hydrolysis of this ester yielded a new trihydroxyhexadecanoic acid, m.p. 140–141° C., $[\alpha]_D$ −10° in methanol, termed ustilic acid B. The substance is further characterized by its infrared spectrum (see Fig. 1) and its hydrazide derivative, m.p. 164–165° C.

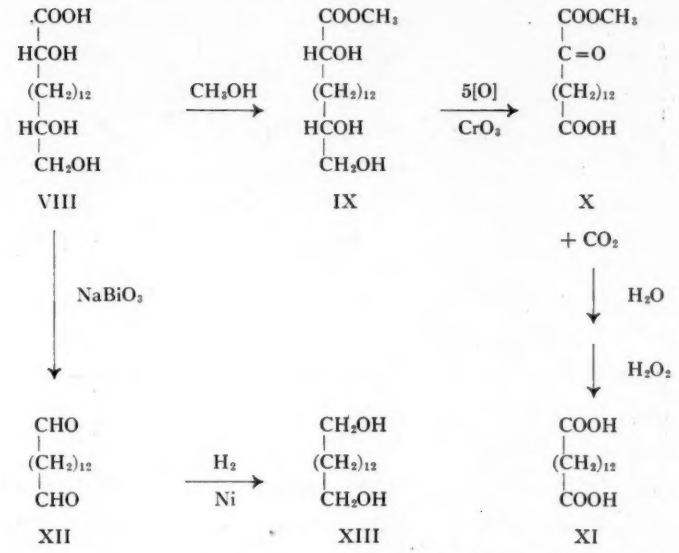
Treatment of ustilic acid A with hydrogen iodide and hydrogenation of the product in alkaline solution in the presence of Raney nickel gave an acid with

a melting point, 59–61° C., which was not depressed by admixture of palmitic acid, m.p. 61.5–62° C. Periodate oxidation of ustilic acid A liberated one mole of formaldehyde, characterized through its methone derivative and determined colorimetrically using chromotropic acid (14). It was thus apparent that ustilic acid A was an optical isomer of 15,16-dihydroxyhexadecanoic acid (I). This conclusion was confirmed by the following observations. Oxidant equivalent to four atoms of oxygen was rapidly consumed on oxidation of methyl ustilate A (II) with chromium trioxide in acetic acid solution. Hydrolysis of the product (III) gave the known pentadecanedioic acid (IV) (4). Oxidation of methyl ustilate A (II) with lead tetraacetate yielded an aldehyde (V) which on hydrogenation gave the methyl ester (VI) (5) of the known 15-hydroxypentadecanoic acid (VII) (3). 15-Hydroxypentadecanohydrazide melted at 142.5–143.5° C.



Oxidant equivalent to five atoms of oxygen was rapidly consumed on oxidation of methyl ustilate B (IX) with chromium trioxide in glacial acetic acid. Hydrolysis of the product (X), m.p. 87–87.5° C., and oxidation with hydrogen peroxide yielded a substance with the composition and melting point of the known tetradecanedioic acid (XI) (4). It was thus apparent that ustilic acid B was an optically active form of 2,15,16-trihydroxyhexadecanoic acid (VIII). This conclusion was confirmed by oxidation of ustilic acid B with sodium bismuthate in glacial acetic acid (28) to the dialdehyde XII which was converted by hydrogenation to a compound with the melting point and composition expected for the known 1,14-dihydroxytetradecane (XIII) (4).

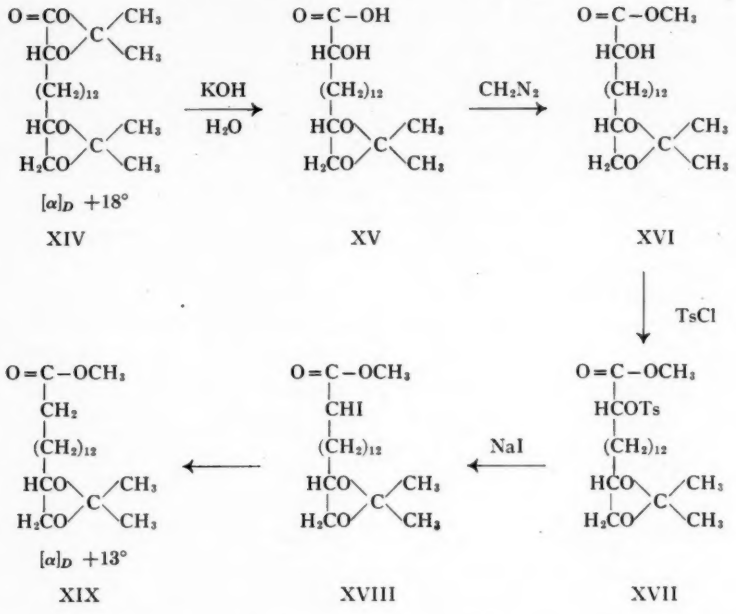
A convenient method for the separation of the ustilic acids was based on the fact that, while ustilic acid A yielded an acidic monoisopropylidene derivative, ustilic acid B yielded a neutral diisopropylidene derivative. The extraction procedure was based on the method used for the determination of the quantity of neutral oil in acidic crude oils described by Jamieson (12).



A mixed melting point curve was determined for the ustilic acids A and B by mixing weighed amounts of the materials and, after grinding the mixture in a mortar, determining its melting point. There was a continual rise in melting point with increasing amount of ustilic acid B such that the melting point curve appeared to be roughly a straight line joining the melting points of the two substances.

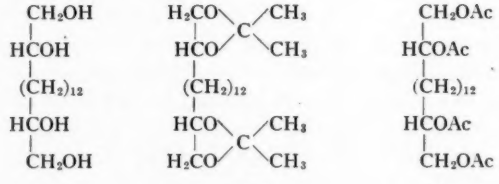
Alkaline hydrolysis of diisopropylideneustilate B (XIV) and methylation of the product (XV) with diazomethane yielded methyl 15,16-isopropylideneustilate B (XVI), m.p. 42.5–43° C., $[\alpha]_D$ +6° in chloroform. Tosylation of XVI and treatment of the product (XVII) with sodium iodide in acetone and hydrogenolysis of the iodocompound formed (XVIII) gave a material from which methyl isopropylideneustilate A (XIX) was prepared. It was thus established that the C15-carbon atoms of the ustilic acids A and B possess identical relative configurations. It is noteworthy that this conclusion is in accord with that expected on the basis of a comparison of the rotations, measured in chloroform, of methyl isopropylideneustilate A (XIX), $[\alpha]_D$ +12°, diisopropylideneustilate B (XIV), $[\alpha]_D$ +18°, and 1,2-isopropylidene-2,15-dihydroxypentadecanoate (XXVIII, see below), $[\alpha]_D$ +5°.

Reduction of diisopropylideneustilate B (XIV) with lithium aluminum hydride and hydrolysis of the product yielded *meso*-1,2,15,16-tetrahydroxyhexadecane (XX), m.p. 133–134° C. The structure of this substance was confirmed by the observation that it rapidly consumed two moles of lead tetraacetate and its optical inactivity was substantiated by the preparation of optically inactive diisopropylidene and tetraacetyl derivatives, XXI and XXII, respectively. Under the conditions of measurement used, XX appeared to be very slightly levorotatory. This observation indicates that the substance



XIV XV XVI XVII XVIII XIX

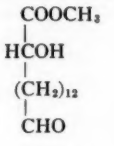
contained an optically active impurity. It is well known that α-hydroxyacids can undergo epimerization relatively easily and it seems likely that the saponification of methyl ustilate B in the preparation of ustilic acid B would be accompanied by the formation of a diastereoisomer which would be extremely difficult to completely separate from ustilic acid B. Therefore, the C2- and C15-hydroxyl groups of ustilic acid B were configurationally *cis* and a Fischer projection formula for ustilic acid B would possess these two hydroxyl groups on the same side of the carbon skeleton.



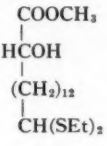
XX XXI XXII

Oxidation of methyl ustilate B (IX) with lead tetraacetate yielded methyl 2-hydroxyaldehydopentadecanoate (XXIII) which was converted to the diethyldithioacetal (XXIV). Reductive desulphurization of the latter compound and hydrolysis of the product gave levorotatory 2-hydroxypentadecanoic acid (XXV), m.p. 89.5–90° C., $[\alpha]_D$ −0.8° in ethanol, which possessed a dextrorotatory sodium salt (see Table I). Hydrogenation of the aldehyde (XXIII) yielded the methyl ester (XXVI), m.p. 74.3–75.3° C., of weakly

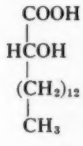
levorotatory 2,15-dihydroxypentadecanoic acid (XXVII), m.p. 102–103° C. Treatment of the latter compound with acetone and sulphuric acid afforded the dextrorotatory isopropylidene derivative XXVIII, m.p. 49–50° C., $[\alpha]_D$ +5° in chloroform.



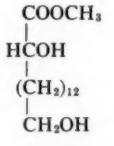
XXIII



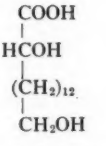
XXIV



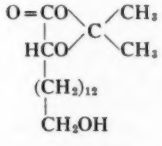
XXV



XXVI

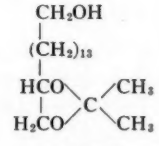


XXVII

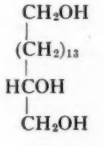


XXVIII

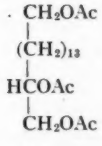
Reduction of methyl isopropylideneustilate A (XIX) with lithium aluminum hydride yielded the dextrorotatory isopropylidene derivative (XXIX), m.p. 60–61° C., $[\alpha]_D$ +12° in chloroform, of levorotatory 1,15,16-trihydroxyhexadecane (XXX), m.p. 108.5–109° C., $[\alpha]_D$ −7° in methanol. The triacetyl derivative (XXXI) of the triol melted at 24–25° C. with $[\alpha]_D$ −0.8° in chloroform.



XXIX

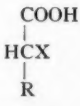


XXX



XXXI

Table I lists the rotations of certain derivatives of the ustilic acids and of related compounds of known configuration. A comparison of these values allows a decision as to the configurations of the ustilic acids. The configurations are assigned on the basis of the conventions for nomenclature which were discussed in an earlier paper in this series (18). Levene and Kuna (21) have pointed out that the molar rotation of a given acid of the general type XXXII, in which X is a functional group and R is an alkyl group, will vary not only with variations in X but also with variations in R. Levene and Marker (22) have shown that the molar rotations of successive members of a configuration-



XXXII

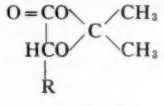
TABLE I

OPTICAL ROTATIONS OF USTILIC ACID DERIVATIVES AND RELATED COMPOUNDS

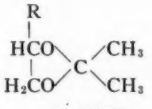
Compound	Mol. wt.	$[M]_D$	°C.	c	Solvent	Reference
A. Free acids						
1. 2L-Hydroxypropanoic	90	+340	25	..	H_2O	21
2. 2L-Hydroxybutanoic	104	+370	25	..	"	21
3. 2L-Hydroxyhexanoic	118	+500	25	..	"	21
4. 2D-Hydroxypentadecanoic	258	−206	..	5	C_2H_5OH	..
5. 2D-Hydroxyhexadecanoic	272	−272	..	5.2	"	13
B. Sodium salts						
1. 2L-Hydroxypropanoate	112	−1400	..	0.84	H_2O	27
2. 2L-Hydroxypentanoate	140	−2040	..	1	"	..
		−2310	..	1	25% C_2H_5OH	..
		−2900	..	1	50% "	..
		−3380	..	1	75% "	..
		−3700	..	1	C_2H_5OH	..
3. 2L-Hydroxyhexanoate	154	−2300	25	..	H_2O	21
4. 2D-Hydroxypentadecanoate	280	+4200	..	1	50% C_2H_5OH	..
C. Hydrazide						
2D,15-Dihydroxypentadecanohydrazide	288	+6930	..	0.2	50% C_2H_5OH	..
D. Isopropylidene lactones						
1. 1,2D,3L,4-Diisopropylidenetetrarate	230	+14,500	17	2.1	$(CHCl_2)_2$	7
2. 1,2-Isopropylidene-2D,15-dihydroxypentadecanoate	314	+1570	..	0.8	$CHCl_3$	..
E. Isopropylidene ketals						
1. 2,3-Isopropylidene-1,2D,3-trihydroxypropane	132	+1430	20	15.2	C_6H_6	1
2. 1,2-Isopropylidene-1,2L,16-trihydroxyhexadecane	314	+2350	..	1	C_6H_6	..

ally related homologous series progressively move in the same direction. Thus, as shown by the first three acids listed in Table I, the molar rotations of the normal α-hydroxyacids increase with increasing molecular weight. It is not possible to state with certainty that the same relationship will hold for the rotations of these acids measured in ethanol. Nevertheless, it seems highly probable that the levorotatory 2-hydroxypentadecanoic acid prepared from ustilic acid B and the levorotatory 2-hydroxyhexadecanoic acid, rotations measured in ethanol, isolated from the wool wax of Merino sheep by Kuwata (13), possessed configurations opposite to the homologous dextrorotatory 2L-hydroxyacids, rotations measured in water. Levene (19) has pointed out that the sodium salts of aldonic acids are more dextrorotatory than the free acids when the 2-carbon atom has the D-configuration and this relationship is well established for the simple 2-hydroxyacids (20,24). As shown in Table I, the molar rotations measured in water of the sodium salts of normal 2-hydroxyacids increase with increasing molecular weight. Also, the molar rotations of sodium 2L-hydroxypentanoate in 0, 25, 50, 75, and 100% aqueous ethanol increased with increase in ethanol concentration. Thus, a comparison of the molar rotation, +4150, of the sodium 2-hydroxypentadecanoate and that, −2900, of sodium 2L-hydroxypentanoate (both measured in 50% ethanol), as well as the fact that the former substance is more dextrorotatory in 50%

ethanol than its free acid in ethanol, indicates that the C2-carbon atoms of the 2-hydroxypentadecanoic acid and its parent substance, ustilic acid B, possessed the D-configuration. Hudson (10) and Levene and Meyer (23) have shown that the phenylhydrazides of aldonic acids with D-C2-carbon atoms are dextrorotatory and Van Marle (29) has shown that this relationship applies to unsubstituted hydrazides when measured in water. Therefore, the dextrorotation, $[M]_D$ +6930°, found for the 2,15-dihydroxypentadecanohydrazide derived from ustilic acid B confirms the above allocation of configuration. The established success of Hudson's Rules of Isorotation (11, p. 17; 16) in the correlation of rotation with configuration for lactol carbon atoms situated in ring structures leaves no doubt that configurationally related homologous compounds such as XXXIII and XXXIV would possess the same sign of rotation. Therefore, the fact, as seen in Table I, that

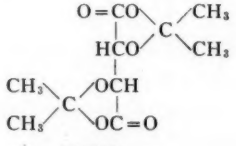


XXXIII



XXXIV

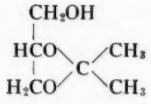
1,2D,3L,4-diisopropylidenetetrarate (XXXV) (7) is dextrorotatory supports the contention that the dextrorotatory 1,2-isopropylidene-2,15-dihydroxy-



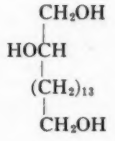
XXXV

pentadecanoate (XXVIII) possessed the D-configuration. These arguments leave no doubt that ustilic acid B was the 2D,15D,16-trihydroxyhexadecanoic acid shown in VIII and that the configurationally related ustilic acid A was the 15D,16-dihydroxyhexadecanoic acid (I). Finally, the fact, as seen in Table I, that 2,3-isopropylidene-1-2D,3-trihydroxypropane (XXXVI) (1) is dextrorotatory indicates that the dextrorotatory 15,16-isopropylidene-1,15,16-trihydroxyhexadecane (XXIX) prepared from ustilic acid A possessed the same relative configuration, a conclusion which is in agreement with the above allocated configurational relationships. It is to be noted, however, that the presently widely accepted rules of nomenclature (6,18) infer that the substance XXX be oriented as shown in XXXVII for purposes of nomenclature. Thus, the asymmetric centers in the substances XXIX, XXX, and XXI, which were derived from 15D,16-dihydroxyhexadecanoic acid, possess the L-configuration. It is noteworthy that the system for nomenclature recently proposed by Cahn and Ingold (2) is free of such aberrations.

The above described separation of the ustilic acids, by distillation of the esterified isopropylidene derivatives, indicated that the mixture contained



XXXVI



XXXVII

approximately twice as much ustilic acid A as ustilic acid B. Treatment of crude ustilic acid, neutral equivalent 296, obtained in quantitative yield from ustilagic acid, with acetone gave a purified ustilic acid mixture with neutral equivalent 293 in 96% yield. The calculated neutral equivalent for a mixture consisting of 70% ustilic acid A and 30% ustilic acid B is 293.2. This indication as to the composition of the ustilic acid mixture was confirmed by the yields of formaldehyde obtained on periodate oxidation of the crude and purified ustilic acid mixtures listed in Table II and by quantitative studies of the rates

TABLE II

FORMATION OF FORMALDEHYDE ON PERIODATE OXIDATION OF USTILIC ACIDS

Time, hr.	Moles of formaldehyde formed per neutral equivalent of ustilic acid			
	Ustilic acid		Ustilic acid mixture	
	A	B	Crude	Purified
1	1.01	1.04	0.98	1.01
2	1.00	1.04	0.99	1.00
4	1.00	1.01	0.99	1.01

of oxidation by chromic oxide in acetic acid of methyl ustilate A, methyl ustilate B, and the mixture of methyl ustilates obtained on treatment of the purified ustilic acid mixture with diazomethane. The results of the latter studies are presented in Fig. 2. It is seen that the initial rapid uptake of oxidant by the methyl ustilates A and B, determined by extrapolation to zero time of the portions of the rate curves corresponding to the slow oxidation by the excess oxidant of the initial products, corresponded to 75.5 gm. (0.25 mole) and 63.6 gm. (0.20 mole) per atom of oxygen consumed, respectively. A similar extrapolation of the rate curve obtained on the oxidation of the methyl ustilate mixture gave a reduction equivalent per atom of oxygen of about 71 gm., the value to be expected if the methyl ustilate mixture were composed of 70% methyl ustilate A and 30% methyl ustilate B.

In a previous publication in this series (17) evidence was provided which indicated that in all probability the ustilagic acid mixture consists almost entirely of monoacetyl-mono-3L-hydroxyhexanoyl (65–70%) and monoacetyl-mono-3L-hydroxyoctanoyl (25–30%) substituted glucoustilic acids. Since the ustilic acid mixture was composed of about 70% ustilic acid A and 30% ustilic acid B, it seems highly probable that the mixture of ustilagic acids is composed essentially of two substances, ustilagic acid A (a monoacetyl-mono-

3L-hydroxyhexanoyl substituted di-β-D-glucosyl-15D,16-dihydroxyhexadecanoic acid) and ustilagic acid B (a monoacetyl-mono-3L-hydroxyoctanoyl substituted di-β-D-glucosyl-2D,15D,16-trihydroxyhexadecanoic acid). It is noteworthy that on the basis of these structures, ustilagic acid A possesses the molecular formula $(C_{2\cdot12}H_{3\cdot65}O)_{17}$ while the molecular formula for ustilagic acid B is $(C_{2\cdot11}H_{3\cdot67}O)_{18}$. This similarity in composition accounts, to a certain degree, for the difficulties encountered in the separation of these substances. The origin of the *n*-caproic acid found in the hydrolyzates of all ustilagic acid preparations (15, 17) remains obscure. Presumably this acid was derived from a third component which made up about 5% of the ustilagic acid mixture.

EXPERIMENTAL

Instrumentation

The infrared spectra and specific rotations were determined as previously described (15). The melting points are corrected.

Crude Ustilic Acid Mixture

Analysis (17) of the ustilagic acid sample used in this work showed it to contain 1.01 acetyl, 0.67 L-3-hydroxyhexanoyl, 0.27 L-3-hydroxyoctanoyl, and 0.05 hexanoyl groups and 1.96 glucose residues per neutral equivalent, 801. The saponification equivalent was 396.

A solution of the ustilagic acid, 13.8 gm. (17.2 me.), in 280 ml. of 4.3% methanolic hydrogen chloride was refluxed for 19 hr. The solution was poured into 600 ml. of water and the aqueous mixture was extracted with chloroform. The chloroform extract was dried and evaporated to a crystalline solid which was dissolved in 100 ml. of ethanol and 40 ml. of 2*N* potassium hydroxide. After the solution was refluxed for two hours, it was poured into 500 ml. of 0.2 *N* hydrochloric acid. The precipitate which formed was gathered by filtration and washed free of chloride with water. After it was dried *in vacuo* at 60° C., the tan-colored material, 5.16 gm. (17.4 me.), neutral equiv. 296, melted at 122–126° C. On the basis that one equivalent of ustilic acids should be obtained per equivalent of ustilagic acid, the yield of crude ustilic acid mixture was 101%.

Purification of the Ustilic Acid Mixture

The above described crude ustilic acid mixture, 590 mgm., was ground to a fine powder and refluxed with 5 ml. of dry acetone. After the mixture was cooled to −10° C., the ustilic acid precipitate was collected by filtration and washed with 5 ml. of cold dry acetone. Evaporation of the acetone filtrates yielded 24 mgm. of a darkly colored residue. Thus, the acetone extraction removed 4% of the ustilic acid mixture. After it was dried *in vacuo* at 60° C., the white ustilic acid mixture, neutral equivalent 293, melted at 123–128° C., with sintering at 120–123° C.

Methyl Ustilate Mixture

The above described purified ustilic acid mixture, 300 mgm., was dissolved in 20 ml. of methanol and the solution was treated with an excess of a freshly distilled ethereal solution of diazomethane. The excess diazomethane was re-

moved by distillation and the solution was evaporated *in vacuo* to a white crystalline solid, m.p. 76–80° C., with sintering at 72–76° C.

Separation of Ustilic Acid Derivatives by Distillation

The above described crude ustilic acid mixture, 4.00 gm., was ground to a fine powder and shaken at room temperature for five hours with 100 ml. of dry acetone and eight drops of concentrated sulphuric acid (26). The ustilic acids, which are only sparingly soluble in acetone, soon dissolved. The yellow-colored solution was poured into a separatory funnel which contained 500 ml. of water and 100 ml. of chloroform. After the mixture was shaken for about 20 seconds, the chloroform layer was separated and washed with 200 ml. of water. The chloroform solution was dried by percolation through a column of dry Celite and evaporated *in vacuo* to a yellow oil which was treated with an excess of an ethereal solution of diazomethane. The ether was removed by distillation and the residue was dried at 0.1 mm. and 100° C. The yellow-colored product which crystallized at room temperature weighed 4.24 gm. and contained 15.3% isopropylidene groups. Fractional distillation of the material, 4.20 gm., at about 0.05 mm. pressure, yielded three fractions. The first fraction, b.p. 133–136° C., weighed 2.52 gm. and contained 12.8% isopropylidene groups. The second fraction was an intermediate fraction, b.p. 136–154° C. which contained 15.4% isopropylidene groups and weighed 0.27 gm. The third fraction distilled at 154–156° C., weighed 1.16 gm., and contained 20.5% isopropylidene groups.

Methyl Isopropylideneustilate A

The first fraction from the above distillation was recrystallized twice from methanol to yield a material, m.p. 46–47° C., $[\alpha]_D$ +12° (*c*, 1.1 in chloroform). Calc. for $C_{20}H_{38}O_4$: C, 70.13; H, 11.18; $(CH_3)_2C$, 12.29%. Found: C, 69.85; H, 11.28; $(CH_3)_2C$, 12.3%.

Diisopropylideneustilate B

After two recrystallizations from methanol, the isopropylidene derivative from the third fraction of the above distillation melted at 42.5–43° C. with $[\alpha]_D$ +18° (*c*, 1.0 in chloroform). Calc. for $C_{22}H_{40}O_5$: C, 68.71; H, 10.49%. Found: C, 68.27; H, 10.48%. Acid hydrolysis liberated acetone equivalent to an isopropylidene group content of 22.0%. Calc. for a diisopropylidene derivative 21.9%. Alkaline hydrolysis liberated acetone equivalent to an isopropylidene group content of 12.3%. Calc. for one alkali-labile isopropylidene group, 10.94%. Absorption characteristic of hydroxyl groups was not present in its infrared spectrum. The substance possessed a strong absorption band at 5.54μ, a considerably shorter wave length than is found for the carbonyl group of acyclic esters of carboxylic acids. For example, methyl isopropylideneustilate A possessed a carbonyl absorption band at 5.88μ.

Methyl Ustilate A

The methyl isopropylideneustilate A, 600 mgm., was treated with 15 ml. of boiling 2% methanolic hydrogen chloride for two hours. The colorless solution was poured into water and the precipitate was extracted with chloro-

form. The dried chloroform extract was evaporated *in vacuo* to a crystalline solid which, after two recrystallizations from methanol, melted at 85.5–86° C. with $[\alpha]_D$ −7° (*c*, 1 in methanol). Calc. for $C_{17}H_{34}O_4$: C, 67.53; H, 11.33%. Found: C, 67.94; H, 11.38%.

Ustilic Acid A

Alkaline hydrolysis of the above described methyl ustilate A yielded a substance, m.p. 112–113° C., $[\alpha]_D$ −8° (*c*, 1 in methanol). Calc. for $C_{16}H_{32}O_4$: C, 66.64; H, 11.19%; neutral equiv. 288.4. Found: C, 66.92; H, 11.22%; neutral equiv. 288. Its infrared absorption spectrum is shown in Fig. 1.

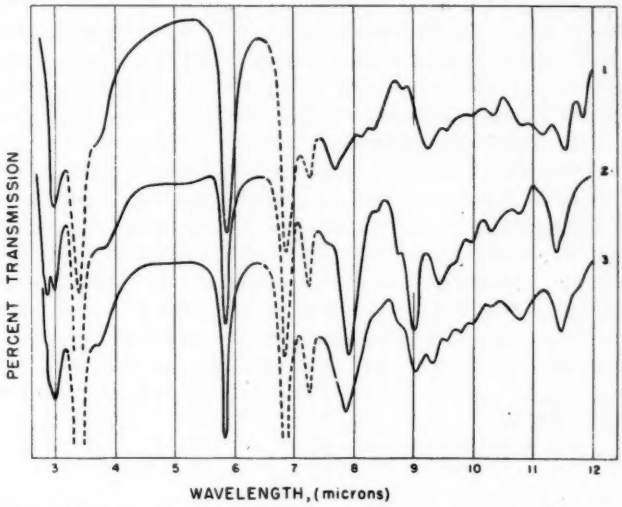


FIG. 1. Infrared spectra. Curve 1, ustilic acid A; Curve 2, ustilic acid B; Curve 3, ustilic acid mixture. – – – – Nujol absorption bands.

Methyl Ustilate B

The diisopropylideneustilate B, 2 gm., was treated with 25 ml. of boiling 2% methanolic hydrogen chloride for two hours. The resulting yellow-colored solution was poured into water, the mixture was extracted with chloroform, and the chloroform extract was washed with water and dried by filtration. The chloroform was removed *in vacuo* to yield a crystalline material which, after three recrystallizations from methanol, melted at 74–75° C. with $[\alpha]_D$ −8.5° (*c*, 1.0 in methanol). Calc. for $C_{17}H_{34}O_5$: C, 64.13; H, 10.76%. Found: C, 64.55; H, 10.91%.

Ustilic Acid B

Alkaline hydrolysis of the above described methyl ustilate B yielded a material, m.p. 140–141° C., $[\alpha]_D$ −10° (*c*, 1.0 in methanol). Calc. for $C_{16}H_{32}O_5$: C, 63.14; H, 10.60%; neutral equiv. 304.4. Found: C, 63.09, 63.27; H, 10.62, 10.27%; neutral equiv. 305. Its infrared absorption spectrum is shown in Fig. 1.

Separation of Ustilic Acid Derivatives by Extraction

A ustilic acid mixture, m.p. 123–128° C., 47.3 gm., was dissolved by being shaken in 500 ml. of dry acetone which contained 5 ml. of concentrated sulphuric acid. The solution was allowed to stand at room temperature for five hours. After this time, the solution was diluted with 800 ml. of Skellysolve C and 800 ml. of ice-cold water was added. The mixture was shaken vigorously for 30 sec., the layers were allowed to separate, and the bottom aqueous layer was withdrawn and discarded. The hydrocarbon layer was washed three times with 200 ml. amounts of water to remove the sulphuric acid and most of the acetone. A cold solution of 20 gm. of potassium hydroxide in 130 ml. of water was then added and the mixture was shaken vigorously for one minute. On the addition of 150 ml. of 50% aqueous ethanol, the emulsion broke and the bottom aqueous layer was separated. The Skellysolve C solution was washed twice with 100 ml. amounts of the 50% ethanol and these extracts were combined with the main aqueous extract. The combined aqueous extracts were extracted with 200 ml. of Skellysolve C and this extract was combined with the main Skellysolve C solution. Chloroform, 150 ml., was added to the combined aqueous layers and this mixture was acidified by the addition of 200 ml. of 2 *N* sulphuric acid. The chloroform layer was washed three times with 100 ml. volumes of water, dried over sodium sulphate and evaporated to a yellow oil which soon crystallized. The yield was 34.8 gm. of crude monoisopropylideneustilic acid A which on hydrolysis gave essentially pure ustilic acid A. The Skellysolve C solution was washed with 50 ml. amounts of water until neutral and dried over sodium sulphate. Evaporation gave 15.1 gm. of a crystalline material which after recrystallization from 25 ml. of methanol melted at 42–42.5° C. Pure diisopropylideneustilate B melted at 42.5–43° C. Hydrolysis yielded essentially pure ustilic acid B.

Palmitic Acid

Methyl ustilate A, 500 mgm., was treated with 10 ml. of boiling 47% hydriodic acid and 2 gm. of red phosphorus for four hours. The reaction mixture was poured into water and the aqueous mixture was extracted with chloroform. The chloroform extract was evaporated to a partially crystalline oil which was dissolved in a mixture of 25 ml. of ethanol, 4 ml. of 10% sodium hydroxide, and 2 ml. of settled Raney nickel catalyst. The mixture was stirred in a hydrogen atmosphere at slightly positive pressure for one hour. The catalyst was removed by filtration and washed several times with boiling water. The combined alcoholic and aqueous filtrates were evaporated to about 75 ml. and the solution was made strongly acid with sulphuric acid. The colorless precipitate was collected by filtration and washed with water. After three recrystallizations from ethanol, the material melted at 59–61° C. and this melting point was not depressed on admixture with an authentic sample of palmitic acid, m.p. 61.5–62° C.

Periodate Oxidation of the Ustilic Acids and Determination of the Formaldehyde Formed

The ustilic acid, 100 mgm., was dissolved in 5 ml. of 0.1 *N* sodium hydroxide

and the solution was made neutral to phenolphthalein with 0.1 *N* sulphuric acid. After the addition of 25 ml. of 0.1 *N* sodium periodate and 25 ml. of water, the mixture was distilled at atmospheric pressure to about 25 ml. volume. In the case of the ustilic acid B the distillate contained a small amount of a steam-distillable, water-insoluble solid which was removed by filtration. In each case, on adding the clear filtrate to 100 ml. of a buffered dimedon solution (25) a precipitate formed which, after isolation and recrystallization from ethanol, possessed, and did not depress, the melting point of the methone derivative of formaldehyde.

A weighed amount of the ustilic acid, 15 to 20 mgm., was dissolved in 20 ml. of 0.1 *N* sodium hydroxide by heating on the steam bath and the cooled solution was diluted to 100 ml. Three 25 ml. aliquots were transferred to 100 ml. flasks and 5 ml. volumes of 0.1 *M* periodic acid were added to each flask. After one, two and four hours, 10 ml. of *N* sulphuric acid and 5 ml. of *M* sodium arsenite solution were added to a flask and the solution was diluted to 100 ml. One milliliter aliquots were transferred to test tubes for development of the chromotropic acid–formaldehyde color reaction in the manner described by Lambert and Neish (14). A standard curve was established by oxidizing, under the above conditions, 5, 10, and 15 ml. volumes of a standard 0.002 *M* solution of mannitol. A reagent blank was used to set the spectrometer at 100% transmittance. The results obtained with the ustilic acids A and B and the above described crude and purified ustilic acid mixtures are shown in Table II.

Rates of Oxidation of Methyl Ustilates by Chromic Oxide

Chromic oxide, 1.00 gm., was dissolved in 2 ml. of water and the solution was diluted to 250 ml. with pure acetic acid. The methyl ustilate, 80–85 mgm., was dissolved in 40 ml. of acetic acid and, at zero time, 50 ml. of the chromic oxide solution was added. The resulting solution was diluted to 100 ml. with acetic acid and, at the various times, 10 ml. aliquots were added to 50 ml. of 0.2 *N* sulphuric acid followed by the addition of about 0.5 gm. of potassium iodide. The liberated iodine was determined by titration with standard sodium thiosulphate solution to the starch end point. The difference in titer between the oxidation mixture and a reagent blank was taken as equivalent to the oxidant consumed by the methyl ustilate. The data plotted in Fig. 2 show that the methyl ustilates A and B rapidly consumed oxidant equivalent to four and five atoms of oxygen, respectively, and that, on this basis, the above described purified methyl ustilate mixture contained about 70% methyl ustilate A and 30% methyl ustilate B.

Pentadecanedioic Acid

Methyl ustilate A, 200 mgm. (0.662 mM.), was dissolved in 5 ml. of glacial acetic acid and 5.30 me. of chromic oxide in 6 ml. of acetic acid was added. After 24 hr. at room temperature, the solution was diluted with 100 ml. of water and the precipitate which formed was gathered by filtration and washed with water. The material was dissolved in 10 ml. of 0.5 *N* sodium hydroxide solution and the mixture was heated on the steam bath for 0.5 hr. The solution

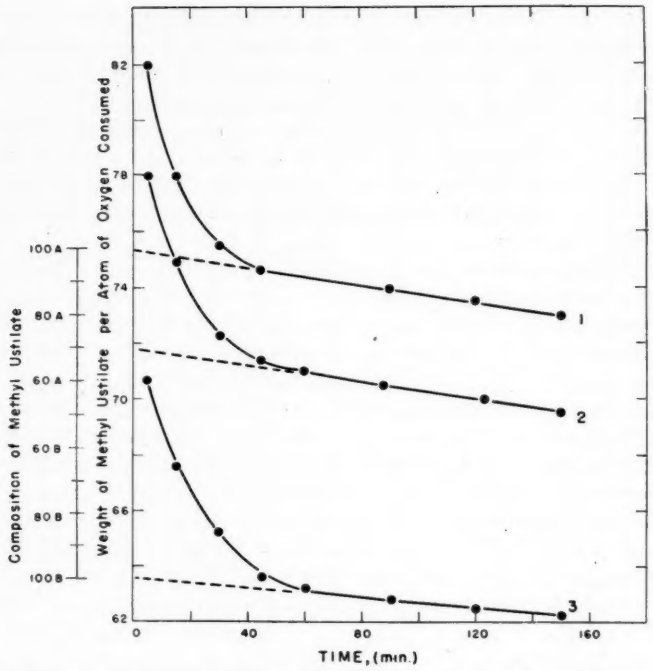


FIG. 2. Oxidation with chromic oxide in acetic acid of methyl ustilate A (Curve 1), methyl ustilate mixture (Curve 2), and methyl ustilate B (Curve 3).

was filtered and acidified with 10 ml. of *N* hydrochloric acid. The precipitate was collected, washed with water, dried, and recrystallized four times from ethyl acetate to yield 71 mgm. of material, m.p. 113–114° C. The melting point recorded for pentadecanedioic acid is 114.6–114.8° C. (4). Calc. for $C_{13}H_{26}(COOH)_2$: C, 66.15; H, 10.36%; neutral equiv., 136.2. Found: C, 66.12; H, 10.36%; neutral equiv., 136.

Methyl 2-Keto-15-carboxypentadecanoate

Chromic oxide, 5.00 gm., in 10 ml. of water was added to 50 ml. of acetic acid and the resulting solution was added to a stirred solution of 3.20 gm. of methyl ustilate B in 50 ml. of acetic acid kept at 0° C. The mixture soon became homogeneous and the solution was kept at 4° C. for 25 hr. The precipitate which had formed on the addition of 250 ml. of water and cooling to 4° C. for three hours was collected and washed with water. The yield was 2.61 gm. of a greenish powder which was extracted with 100 ml. of boiling Skellysolve C. On cooling the extract, 1.96 gm. of a white crystalline solid, m.p. 71–74° C., was deposited. Recrystallization from two parts acetone gave 1.74 gm., m.p. 84.5–86°C. Three further recrystallizations from acetone gave a nicely crystalline product, m.p. 87–87.5° C. This ester, like other α-keto esters, was highly susceptible to alkaline hydrolysis and it was not possible to determine the

neutral equivalent by direct titration. Titration of an alcoholic solution with 0.1 *N* aqueous sodium hydroxide to phenolphthalein indicator gave a combined neutral and saponification equivalent of 150.5. Calculated, 150.2. Calc. for $C_{16}H_{28}O_5$: C, 63.98; H, 9.39%. Found: C, 64.13; H, 9.55%.

Tetradecanedioic Acid

The monomethyl ester of 2-ketopentadecanedioic acid, 230 mgm., was hydrolyzed to yield 217 mgm. of the 2-ketopentadecanedioic acid as a white powder which was not purified. The material, 200 mgm., was stirred at room temperature with 10 ml. of 30% hydrogen peroxide (13) for 20 hr. The resulting material was washed with water and air-dried. After recrystallization, first from 70% ethanol, then twice from ethyl acetate, and once more from 70% ethanol, the yield was 68 mgm., m.p. 124.5–125° C. Tetradecanedioic acid is reported (4) to melt at 125.8° C. Calc. for $C_{14}H_{26}O_4$: C, 65.06; H, 10.14%; neutral equiv., 129.2. Found: C, 65.20; H, 10.11%; neutral equiv., 129.

1,14-Dihydroxytetradecane

Ustilic acid B, 3.18 gm. (10.5 mM.), was suspended in 45 ml. of acetic acid and the stirred mixture was heated to 45° C. Commercial sodium bismuthate (28), about 80% pure, 7.50 gm. (about 21.5 mM.), was added over a period of 20 min. and the reaction mixture, kept in a nitrogen atmosphere, was stirred for a total of 40 min. Benzene, 50 ml., and water, 45 ml., were added and, after vigorous shaking, the aqueous layer was withdrawn and re-extracted with 50 ml. of benzene. The benzene extracts were washed with 20 ml. of 50% aqueous acetic acid, combined, and washed free of acetic acid with water. After it was dried over sodium sulphate the solution was filtered and evaporated *in vacuo* to an oil which hardened at room temperature. The material, which was extremely prone to auto-oxidation, was dissolved in 50 ml. of ethanol and hydrogenated at 1500 p.s.i. for four hours at 100° C. using Raney nickel catalyst. The catalyst was removed by filtration and the filtrate was evaporated *in vacuo* to a crystalline solid which was triturated with low-boiling petroleum ether to yield 2.19 gm. of a faintly greenish-tinted material, m.p. 78–82° C. Distillation at 10^{-2} mm. pressure gave 1.81 gm., m.p. 83–85° C., of a substance which melted at 85–86° C. after one recrystallization from benzene. Chuit (4) has reported 1,14-dihydroxytetradecane to melt at 84.8° C. Calc. for $C_{14}H_{30}O_2$: C, 72.96; H, 13.12. Found: C, 72.95; H, 13.08. The crude yield was 91%.

Lead Tetraacetate Oxidations

About 0.25 mM. of the compound was dissolved in 5 ml. of acetic acid, 15 ml. of 0.13 *N* lead tetraacetate in glacial acetic acid solution was added, and the solution was diluted to 25 ml. After one and two hours, the excess oxidant in 10 ml. aliquots was determined in the usual manner (9). Both methyl ustilate A and methyl ustilate B consumed one mole of oxidant per mole of ester.

15-Hydroxypentadecanoic Acid

Methyl ustilate A, m.p. 84–85° C., 4.19 gm., was dissolved in 80 ml. of

acetic acid and 8 gm. of lead tetraacetate was added. The reaction mixture was shaken until homogeneous and left at room temperature for one hour. Benzene, 50 ml., was added and the mixture was poured into 200 ml. of water which contained a little glycerol to destroy the excess oxidant. After vigorous shaking, the water layer was withdrawn and re-extracted with 25 ml. of benzene. The combined benzene extracts were washed with water until free of acetic acid and evaporated to an oil which soon crystallized. This substance, methyl aldehydopentadecanoate, could not be obtained in a highly pure condition because of its strong tendency to undergo auto-oxidation and was hydrogenated directly at 1500 p.s.i. for two hours at 100° C. over Raney nickel catalyst in 75 ml. of ethanol. The catalyst was removed by filtration and the ethanol solution was evaporated to yield 3.70 gm., 98% yield, of a crystalline solid, m.p. 48–51° C. Recrystallization from one part methanol gave pure methyl 15-hydroxypentadecanoate, m.p. 51.5–52° C. Calc. for $C_{16}H_{32}O_3$: C, 70.56; H, 11.84%. Found: C, 70.11; H, 11.63%. Chuit and Hausser (5) reported this substance to melt at 52–52.5° C. Alkaline hydrolysis of this ester gave an acid which after three recrystallizations from ether melted at 84.5–85° C. 15-Hydroxypentadecanoic acid is reported (5) to melt at 84° C. Calc. for $C_{15}H_{30}O_3$: C, 69.74; H, 11.70%; neutral equiv., 258.4. Found: C, 69.66; H, 11.97%; neutral equiv., 259.

Methyl 2D,15-Dihydroxypentadecanoate

Methyl ustilate B, m.p. 73–74° C., 1.92 gm., was dissolved in 60 ml. of acetic acid and 3.2 gm. of lead tetraacetate was added. The mixture was shaken until homogeneous and left at room temperature for one hour. The methyl 2-hydroxyaldehydopentadecanoic acid which formed was isolated as described above. The crude crystalline product was hydrogenated at 1500 p.s.i. for three hours at 100° C. over Raney nickel catalyst in 25 ml. of ethanol. The catalyst was removed by filtration and the filtrate was evaporated *in vacuo* to a crystalline solid, 1.57 gm., 90% yield, m.p. 68–72° C. Several recrystallizations from two parts methanol gave pure methyl 2D,15-dihydroxypentadecanoate, m.p. 74.3–75.3° C. Calc. for $C_{16}H_{32}O_4$: C, 66.64; H, 11.19%. Found: C, 66.80; H, 10.96%.

2D,15-Dihydroxypentadecanoic Acid

Alkaline hydrolysis of the above described ester gave a substance which melted at 102–103° C. after three recrystallizations from methanol and which was very weakly levorotatory in methanol. Calc. for $C_{15}H_{30}O_4$: neutral equiv., 274.4. Found: neutral equiv., 275.

1,2-Isopropylidene-2D,15-dihydroxypentadecanoate

The dihydroxyacid, 80 mgm., was treated with 5 ml. of dry acetone and two drops of sulphuric acid for 20 hr. at room temperature. The product, isolated in the usual manner, was recrystallized from ligroin to yield 62 mgm. of material, m.p. 49–50° C., with $[\alpha]_D$ +5° (*c*, 0.8 in chloroform). Calc. for $C_{18}H_{34}O_4$: C, 68.75; H, 10.90%. Found: C, 69.43; H, 11.06%.

2D-Hydroxypentadecanoic Acid

Crude methyl 2D-hydroxyaldehydopentadecanoate, prepared as described

above from 1.90 gm. of methyl ustilate B, was dissolved at 0° C. in 10 gm. of ethyl mercaptan which contained 1.0 gm. of anhydrous zinc chloride (30). The solution was kept at 4° C. for four hours and poured into 100 ml. of aqueous sodium bicarbonate solution. The precipitate, collected by filtration, was extracted three times with boiling chloroform and the combined chloroform extracts were used to extract the aqueous phase. The chloroform solution was dried over sodium sulphate and evaporated *in vacuo* to an oil, which was dried *in vacuo* at 60° C. Calc. for $C_{20}H_{40}O_3S_2$: C, 61.18; H, 10.27%. Found: C, 60.99; H, 10.46%. The substance, n_D^{25} 1.4890, was dissolved in 50 ml. of ethanol containing 40 ml. of settled Raney nickel, and the mixture was refluxed for 2.5 hr. The catalyst was collected by filtration and twice extracted with 50-ml. amounts of ethanol. The combined ethanolic solutions were evaporated *in vacuo* to an oil which crystallized at room temperature. The substance was distilled to yield a 1.21 gm. fraction, b.p. 117–118° C. at about 0.05 mm., which melted at 23–29° C. Alkaline hydrolysis of the material, 1.12 gm., saponification equivalent 260, gave an acidic product which was dissolved in 5 ml. of chloroform and petroleum ether was added to turbidity. On cooling, there crystallized 0.99 gm. of a substance, m.p. 88–89° C. Three recrystallizations from three parts 90% methanol gave a substance, m.p. 89.5–90° C., $[\alpha]_D$ −0.8° (*c*, 5 in ethanol). Calc. for $C_{15}H_{30}O_3$: C, 69.74; H, 11.70%; neutral equiv., 258.4. Found: C, 69.39; H, 11.12%; neutral equiv., 258.

Sodium 2D-hydroxypentadecanoate

2D-Hydroxypentadecanoic acid, 130 mgm., was dissolved in 15 ml. of ethanol and the solution was neutralized to phenolphthalein with 0.1 *N* sodium hydroxide solution. Evaporation gave a solid which was recrystallized first from 50% ethanol then from pure ethanol to yield 101 mgm. of a nicely crystalline product, $[\alpha]_D$ +15° (*c*, 1 in 50% aqueous ethanol). Calc. for $C_{15}H_{29}O_3Na$: C, 64.26; H, 10.43%. Found: C, 64.11; H, 10.23%.

Sodium 2L-Hydroxypentanoate

The previously described (18) methyl 2L-hydroxypentanoate, $[\alpha]_D$ +16.6° (*c*, 1.2 in chloroform), 446 mgm., was heated on the steam bath for one hour with 35 ml. of 0.1 *N* sodium hydroxide. The neutral solution was evaporated to a crystalline solid which was dissolved in 20 ml. of ethanol. On the addition of 40 ml. of dry acetone and cooling to −8° C., there crystallized 300 mgm. of the salt in a nicely crystalline condition. The substance was not very hygroscopic. Calc. for $C_5H_9O_3Na$: H, 6.47%. Found: H, 6.54%. The rotations for this substance are given in Table I.

15D,16-Dihydroxyhexadecanohydrazide (Ustilohydrazide A)

Methyl ustilate A, 0.5 gm., was heated under reflux for 30 min. with 0.5 ml. of hydrazine hydrate and 1 ml. of ethanol. Four milliliters of ethanol was added and the heating was continued for 30 min. On cooling, a near quantitative yield of the hydrazide crystallized. After recrystallization from ethanol the substance melted at 140.5–141.5° C. Calc. for $C_{16}H_{34}O_3N_2$: C, 63.54; H, 11.33%. Found: C, 63.59; H, 10.74%.

2D,15D,16-Trihydroxyhexadecanohydrazide (Ustilohydrazide B)

This substance, prepared as described above and purified by recrystallization

from ethanol, melted at 164–165° C. Calc. for $C_{16}H_{34}O_4N_2$: C, 60.34; H, 10.76%. Found: C, 60.27; H, 10.68%.

2D,15-Dihydroxypentadecanohydrazide

This substance, prepared as described above and purified by recrystallization from ethanol, melted at 129–130° C. with $[\alpha]_D$ +24° (*c*, 0.2 in 50% aqueous ethanol) measured in a 4 dm. tube. Calc. for $C_{15}H_{32}O_3N_2$: C, 63.14; H, 11.19%. Found: C, 63.28; H, 11.22%.

15-Hydroxypentadecanohydrazide

This substance, prepared as described above and purified by recrystallization from ethanol, melted at 142.5–143.5° C. Calc. for $C_{15}H_{32}O_2N_2$: C, 66.15; H, 11.84%. Found: C, 66.06; H, 12.18%.

Meso-1,2,15,16-tetrahydroxyhexadecane

Diisopropylidene ustilate B, m.p. 42.5–43° C., 3.84 gm. (10 mM.), was dissolved in 50 ml. of dry ether and an excess of an ethereal solution of lithium aluminum hydride was added. After the solution had been allowed to stand at room temperature for two hours, it was poured into ice-water and acidified with 10% sulphuric acid. The resulting mixture was extracted twice with chloroform and the filtered extract was evaporated to a crystalline solid. The material was dissolved in 25 ml. of ethanol and 10 ml. of 0.1 *N* hydrochloric acid was added. After the solution had been boiled for 15 min., 20 ml. of water was added and the solution was kept at 4° C. for two hours. The crystalline precipitate, 2.89 gm., 95% yield, melted at 127–130° C. After one recrystallization from methanol, the yield was 2.70 gm., m.p. 132–134° C. Further recrystallizations from methanol or acetic acid did not raise the melting point above 133–134° C. The material was insoluble in ethyl acetate, chloroform, ether, or water and only sparingly soluble in cold pyridine, acetic acid, methanol, or ethanol. The substance appeared to possess a slight optical activity, $[\alpha]_D^{40} < -0.5°$ (*c*, 1 in methanol). Calc. for $C_{16}H_{34}O_4$: C, 66.18; H, 11.80%. Found: C, 66.15; H, 11.46%. Oxidation with an excess of lead tetraacetate in acetic acid resulted in the consumption of 2.0 moles of the oxidant after one- and two-hour reaction times.

Diisopropylidene-meso-1,2,15,16-tetrahydroxyhexadecane

The 1,2,15,16-tetrahydroxyhexadecane, m.p. 133–134° C., 500 mgm., was suspended in 20 ml. of dry acetone which contained two drops of sulphuric acid. After the mixture had been shaken for one hour, solution was complete. The mixture was left at room temperature overnight and poured into 100 ml. of aqueous bicarbonate solution. The material, which crystallized immediately, was gathered by filtration and washed with water. The yield was 630 mgm., 99%, m.p. 65–66° C. Recrystallization from methanol gave a pure product, m.p. 66.5–67° C., which was optically inactive (*c*, 1.5 in chloroform). Calc. for $C_{22}H_{42}O_4$: C, 71.29; H, 11.42%. Found: C, 70.98; H, 11.81%.

Meso-1,2,15,16-tetraacetoxyhexadecane

Meso-1,2,15,16-tetrahydroxyhexadecane, 240 mgm., was heated on the

steam bath for one hour with 10 ml. of acetic anhydride and 200 mgm. of sodium acetate. The mixture was stirred overnight with 100 ml. of water. The crystalline precipitate which had formed was washed with water and dried. The yield was 380 mgm., 100%, m.p. 79–80° C. Recrystallization from methanol gave coarse crystals, m.p. 79.5–79.7° C., of an optically inactive substance (*c*, 1.5 in chloroform). Calc. for $C_{24}H_{42}O_8$: C, 62.87; H, 9.23%. Found: C, 62.87; H, 9.15%.

1,2-Monoisopropylidene-1,2L,16-trihydroxyhexadecane

Methyl isopropylideneustilate A, 1 gm., was dissolved in 25 ml. of ether and the solution was treated with an excess of an ethereal solution of lithium aluminum hydride. After 0.5 hr. at room temperature, the solution was poured into 50 ml. of ice-water which contained 2 ml. of acetic acid and the mixture was extracted several times with ether. The ether extracts were combined, washed with water, dried over sodium sulphate, and evaporated to a crystalline solid. Recrystallization from ligroin gave 590 mgm. of a substance, m.p. 60–61° C., $[\alpha]_D$ +7.5° (*c*, 1 in benzene) and +12° (*c*, 1 in chloroform). Calc. for $C_{19}H_{38}O_3$: C, 72.49; H, 12.18%. Found: C, 72.42; H, 12.05%.

1,2L,16-Trihydroxyhexadecane

Acid hydrolysis of the above described isopropylidene derivative, 225 mgm., yielded 190 mgm. of product, m.p. 107.5–108.5° C. After two recrystallizations from methanol, the material melted at 108.5–109° C. with $[\alpha]_D$ −7° (*c*, 1 in methanol). Calc. for $C_{16}H_{34}O_3$: C, 70.04; H, 12.49%. Found: C, 70.52; H, 12.28%.

1,2L,16-Triacetoxyhexadecane

Acetylation of the above described 1,2L,16-trihydroxyhexadecane, 80 mgm., with acetic anhydride and sodium acetate and isolation of the product which crystallized on decomposing the reaction mixture with water gave 105 mgm., 90% yield, of a low melting compound. After recrystallization from 30–40 petroleum ether, the material melted at 24–25° C. with $[\alpha]_D$ −0.8° (*c*, 1 in chloroform). Calc. for $C_{22}H_{40}O_6$: C, 65.97; H, 10.07%. Found: C, 66.19; H, 10.20%.

Conversion of Ustilic Acid B to Ustilic Acid A

Diisopropylidene ustilate B, 2.56 gm., was dissolved in 20 ml. of ethanol and 5 ml. of 2 *N* potassium hydroxide was added. The solution was refluxed for 30 min., diluted with 40 ml. of water, 35 ml. of chloroform, and 15 ml. of *N* hydrochloric acid. After shaking, the chloroform layer was isolated and washed twice with water, dried over sodium sulphate, and evaporated to a crystalline solid. The material was treated with an excess of diazomethane in ether, the ether was removed by evaporation, and the residue was dissolved in 5 ml. of methanol. The solution was filtered and diluted with water to turbidity. On cooling there crystallized 2.19 gm., 92%, of methyl 15,16-isopropylideneustilate B, m.p. 42–43° C. After recrystallization from ligroin, the material melted at 42.5–43° C. with $[\alpha]_D$ +6° (*c*, 1 in chloroform). Calc. for $C_{20}H_{38}O_5$: C, 67.00; H, 10.68%. Found: C, 67.38; H, 10.50%. This material,

1.68 gm., was dissolved in 10 ml. of dry pyridine which contained 1.60 gm. of *p*-toluenesulphonyl chloride and the solution was left at room temperature for two days. The mixture was stirred with 50 ml. of 50% aqueous acetone for 30 min. and extracted with chloroform. The chloroform extract was washed several times with water and evaporated to an oil which did not crystallize. The oil was dissolved in 25 ml. of dry acetone which contained 10 gm. of sodium iodide and the mixture was heated at 140° C. for five hours. The reaction mixture was poured into 50 ml. of water and the free iodine was reacted with sodium thiosulphate. Extraction with chloroform gave a brown-colored oily product which gave a strong test for iodine. The substance was dissolved in 25 ml. of ethanol containing 10 ml. of 2 *N* aqueous sodium hydroxide and about 2 ml. of Raney nickel catalyst. The solution was hydrogenated for two hours at 1000 p.s.i. pressure. After removal of the catalyst, the solution was concentrated to about 10 ml., acidified with hydrochloric acid to Congo red indicator, and the solid precipitate was washed with water, dried at 65° C. *in vacuo*, and dissolved in 25 ml. of dry acetone which contained four drops of concentrated sulphuric acid. The solution was left at room temperature for seven hours, diluted with 50 ml. of chloroform, and the mixture poured into 50 ml. of water. After shaking, the chloroform layer was isolated and washed several times with water, dried over sodium sulphate, and evaporated *in vacuo* to yield a brown-colored oil which was treated with an excess of diazomethane in ether. Solvent removal gave an oil which was distilled at about 0.1 mm. to yield a 463 mgm. fraction, b.p. 140–143° C. The substance, $[\alpha]_D$ +13° (*c*, 1 in chloroform), melted at 46–47° C. and a mixed melting point with methyl isopropylideneustilate A, m.p. 47–47.5° C., was 46–47.5° C. The over-all yield from methyl 15,16-isopropylideneustilate B was 29%. Methanolysis to remove the isopropylidene group gave methyl ustilate A, m.p. 85–86° C.

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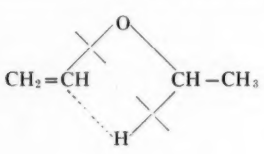
THE KINETICS OF THE THERMAL DECOMPOSITION OF VINYL ISOPROPYL ETHER[1]

By Arthur T. Blades

ABSTRACT

The thermal decomposition of vinyl isopropyl ether in the presence of toluene has been studied in a flow system in the temperature range 447-521°C. In this range, the data indicate a purely intramolecular decomposition into propylene and acetaldehyde, the activation energy for the reaction being in close agreement with that found for the decomposition of vinyl ethyl ether. At 570°C. a minor free radical decomposition of the ether becomes apparent. Some qualitative studies of the decomposition of vinyl isobutyl ether are also reported.

Recent studies of the decomposition of vinyl ethyl ether (1, 4) indicate a simple intramolecular split into ethylene and acetaldehyde as the major reaction. Two possible mechanisms have been suggested (4) for this decomposition, both of which involve cyclic transition states.



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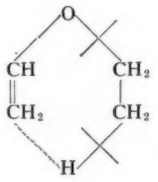


II

The Type I transition state was supported by Wang and Winkler (4) on the basis of energy considerations, while the Type II has gained support from the comparison of the entropy of activation with that for the rearrangement of vinyl allyl ether (3). Since the predicted products from vinyl isopropyl ether depend on the mechanism of the decomposition, further support for one of these transition states may be obtained from its pyrolysis, the assumption being made that a similar transition state applies for both ethers.

EXPERIMENTAL

Vinyl isopropyl ether (stabilized with 0.01% phenyl α-napthyl amine) was donated by the Ohio Chemical Company and was distilled over calcium oxide on a 10 plate column b.p. 54.7 (741 mm.) $n_D^{25} = 1.3841$.

Vinyl isobutyl ether (stabilized) was purchased from General Aniline and Film Corp. and distilled b.p. 81.4 (740 mm.) $n_D^{25} = 1.3938$.

The toluene was Merck and Company Reagent Grade and was distilled over sodium on the same column.

The apparatus was similar to that described previously. The reacting gas, consisting of toluene and the ether in a molar ratio of about thirty to one, passed through a 1.8 cm. diameter, 20 cm. long, quartz reaction cell maintained

[1] *Manuscript received December 5, 1952.*
Contribution from the Chemistry Department of the University of Wisconsin, Madison, Wis.

to ± 0.2° in an aluminum bronze block furnace. The temperature was continuously monitored on a Brown Recording Potentiometer from a triple junction chromel – P alumel thermocouple. The pressures were measured frequently during a run on an oil–mercury manometer with a magnification factor of 10. The effluent gases were forced to pass through a flow limiting capillary and were then condensed in dry ice – acetone and liquid air traps. Permanent gases were collected by an automatic Toepler pump and analyzed on a modified Haden and Luttropp (2) type apparatus.

Vinyl Isopropyl Ether

The main products of this decomposition with and without toluene as the carrier gas were shown by infrared analyses to be propylene and acetaldehyde. The presence of toluene served to prevent the production of permanent gases (carbon monoxide, methane, hydrogen) over the complete temperature range (447-521°C.) of the kinetic study. At 570°C., however, very small quantities of equal proportions of hydrogen, carbon monoxide, and methane, and traces of bibenzyl were also produced when toluene was used as the carrier gas.

Rate measurements were made by aldehyde analyses using a Beckman Spectrophotometer at 302, 305, and 310 mμ where the acetaldehyde absorbs strongly but the ether is transparent.

By varying the contact time from 0.34-1.1 sec. the decomposition into acetaldehyde and propylene was shown to obey a first order rate law (Table I, R. 14, 15, 16, 17, and 18).

TABLE I

RATE STUDIES IN THE PRESENCE OF TOLUENE

Run No.	Total moles	Pressure, cm. Hg	Contact time, sec.	% Decomposition	k, sec.$^{-1}$	T, °K.
2	.0570	1.88	0.523	87	3.92	794.6
A (Av. of 9 runs)				—	2.93	785.7
21	.0545	1.90	0.571	62	1.70	770.3
13	.0898	1.74	0.324	23	0.812	751.9
14	.0883	1.76	0.336	19	0.620	746.4
15	.0430	2.04	0.804	43	0.689	745.8
16	.0337	2.15	1.08	50	0.650	746.3
17	.0836	1.96	0.594	33	0.671	746.4
18	.0828	1.93	0.596	32	0.648	745.3
19	.0690	1.93	0.600	23	0.428	734.8
22	.0457	2.09	1.10	24	0.254	722.6
20	.0827	1.91	0.607	14	0.250	720.2

The data conform to the Arrhenius equation as may be seen from Fig. 1 and

$$k = 3.8 \times 10^{12} \exp(-43{,}560/RT) \text{ sec.}^{-1}$$

When compared with the Absolute Rate Theory equation

$$k = \kappa \frac{k'T}{h} e^{\Delta S^{\ddagger}/R} e^{-\Delta H_a/RT}$$

a value of $\Delta S^{\ddagger} = -4.8$ e.u. at 760°K. is obtained if the transmission coefficient κ is assumed to be unity.

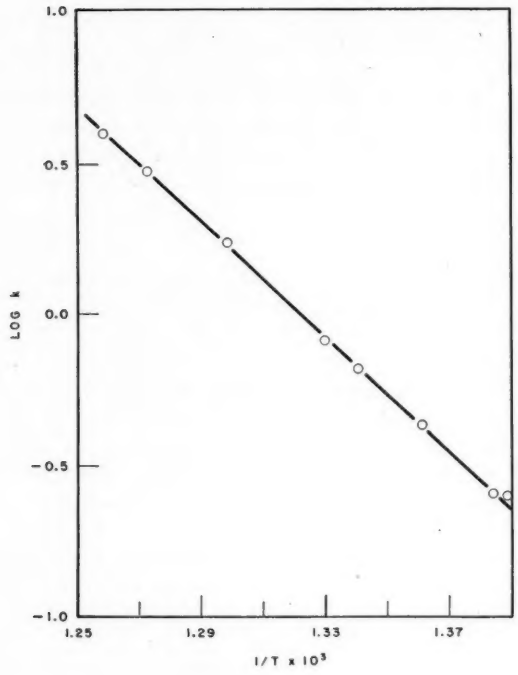


FIG. 1.

The quantities of permanent gases produced proved to be too small to make any measurements on their rate of production.

Vinyl Isobutyl Ether

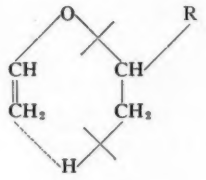
Preliminary studies of the decomposition of vinyl isobutyl ether indicate that the major products are acetaldehyde and isobutene as identified by boiling points and infrared spectra. In addition, however, small quantities of propylene and propionaldehyde were also identified along with fairly large quantities of permanent gases.

When the decomposition was carried out in the presence of toluene, these permanent gases were found to consist of about 25% carbon monoxide, 2-5% hydrogen, and the remainder methane. No attempt was made to identify the liquid products in the presence of toluene.

DISCUSSION

The production of acetaldehyde and the corresponding alkene in the pyrolysis of isopropyl and isobutyl vinyl ethers rather than the products predicted by transition state I lends considerable support to the Type II for the decomposition of vinyl ethyl ether. In addition, the similarity of the activation energies (43.8 and 43.56 kcal. per mole) found for the ethyl and isopropyl vinyl ether

decompositions strongly suggests that both take place via a similar transition state.



The negative entropy of activation found for the vinyl isopropyl ether is also consistent with a cyclic transition state since three internal rotational degrees of freedom are frozen out in the process of activation. The large difference in the entropies of activation of ethyl (− 10.2 e.u. at 530°C.) and isopropyl (− 4.8 e.u. at 490°C.) vinyl ether can presumably be explained on the basis of the restriction of internal rotation due to the presence of an extra methyl group in isopropyl vinyl ether.

The simultaneous occurrence of the permanent gases and the traces of bibenzyl in the decomposition of vinyl isopropyl ether suggests that these gases arise from an initial free radical decomposition of the ether, presumably into the vinyloxy and isopropyl radicals. The meager data available, however, add little to the understanding of this mode of decomposition.

The permanent gases collected in the decomposition of vinyl isobutyl ether in the presence of toluene are not entirely as would be predicted from the above mechanism; no attempt has been made to explain this anomaly.

The author wishes to thank Mr. D. Johnson for the infrared analyses, Dr. G. W. Murphy for many inspiring discussions, and the University Research Committee for support from funds supplied by the Wisconsin Alumni Research Foundation.

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THE ELECTROLYTIC POLISHING OF AMPHOTERIC METALS[1]

By E. J. Casey and R. E. Bergeron

ABSTRACT

Experimental determinations of conditions necessary for the electrolytic polishing of amphoteric metals in alkali hydroxide solutions are described. The effects of temperature, electrolyte concentration, current density, and time of current flow are presented, as are differences among lithium, sodium, and potassium hydroxide solutions. Interpretation of the results in terms of a theory involving anodic polarizations has indicated the importance of the formation and maintenance of an anodic film whose electrical and mechanical properties determine critically the nature of the surface resulting from anodic treatment. Further applications of such studies toward the elucidation of mechanisms of anodic processes are indicated.

INTRODUCTION

In the past few years electrolytic methods of finishing metal surfaces have assumed considerable practical importance. Mechanical polishing has its disadvantages: for instance, the friction between metal piece and polishing wheel results often in "flow" of the metal surface, resulting in cold working and deformation of the metallic surface. In some cases certain parts of the metallic piece are impossible to polish because of shape. In the case of very hard metals, the useful life of the polishing wheel is short. About 1935 serious consideration began to be given to an electrolytic method of polishing. The specimen is made the anode in an electrochemical cell, and under certain fairly critical conditions the burrs and rough spots are stripped from the surface. The necessary conditions seem to be (*a*) a high polarization at the anode, whether in the form of true concentration polarization of the anode (2, 8, 9) or as an adsorbed layer on the anode surface (5, 17), (*b*) a fairly high viscosity of the electrolyte, (*c*) high viscosity of anode layer (17), (*d*) ability of the electrolyte to dissolve the reaction products; (*e*) and at the same time the practical considerations of high enough current density to effect the polishing in reasonable time.

Many methods are described in both the patent (3) and nonpatent literature for electrolytic polishing of metals, for example the reviews of Faust (3), Jacquet (10), and Zmeskal (18). Stress has been placed of course on media for polishing steels. Usually the electrolyte used is some combination of glycerol, sulphuric acid, phosphoric acid, acetic acid, acetic anhydride, chromic acid, hydrochloric acid, hydrofluoric acid—in general, strongly acidic solutions. However, other methods involve slightly acid, neutral, and even slightly alkaline media (pH 10)—sodium cyanide, sodium orthophosphate, and sodium pyrophosphate.

Although alkaline solutions would seem to be ideal media for polishing the amphoteric metals—those whose gelatinous hydroxides manifest acidic as well as basic properties—very little work has been done along this line.

[1] *Manuscript received November 6, 1952.*
Contribution from the Electrochemistry Laboratory, Defence Research Chemical Laboratories, Ottawa, issued as D.R.C.L. Report No. 113.

Vernon and Stroud (16) report electropolishing of zinc in 25% of potassium hydroxide at a critical current density. Kerr (11) noticed the formation of brown anodic films on tin in sodium hydroxide solution; analysis of these showed oxides of tin to be present. Shepherd (13) has found that the X-ray diffraction pattern of the dried anodic film formed on zinc in potassium hydroxide is characteristic of zinc oxide. Huber's electron and X-ray diffraction work (6) has indicated that anodization of magnesium, cadmium, and zinc produces as the primary product, magnesium oxide, cadmium oxide, and zinc oxide respectively on the surface. Indications are that the resistance of such tightly bound films may be very high.

It is the purpose of this paper to present, analyze, and discuss some experimental work which provides considerable information on the nature of the electropolishing phenomenon and on the mechanism of anodic reactions in general.

THEORY

Consider the small volume just on the solution side of the electrode–solution interface, a volume with cross-sectional area equal to the planar, apparent area of the electrode, and having an average depth of a few hundred microns. If the electrode is made the anode, metal ions are liberated into this surface layer compartment of the solution. Chemical reactions or ionic associations may follow, producing an increased concentration of metal ion compounds in the layer, even to the extent, in some cases, of exceeding the solubility of some soluble salt (17). The composition of the layer and the exact nature of the compounds thus formed critically determine such electrical and mechanical properties of the layer as: mechanical strength, or extent and nature of cross-bonding; the viscosity of the layer; the conductivity and diffusion coefficient of charged and uncharged particles in the layer. If the layer is insoluble in the bulk solution, resistance polarization is soon so high that very little current can flow, even with high impressed terminal voltage. If the layer is soluble in the bulk solution, the steady state thickness and composition of the film will be determined by (1) the nature and extent of the solubility of the film in the bulk solution, (2) the rate of solution, (3) the diffusion of various reactants and products through this layer toward or away from the anode under the steady-state concentration gradients. A further factor enters at high current density. If the rate of removal of the soluble film is too slow, the metal ions will pile up at the anode producing a back-e.m.f. of concentration polarization: then in order that the chosen current pass, the terminal voltage must be raised above that necessary for the discharge of water or OH^-, and oxygen is released. The vigorous stirring thus provided completely changes again the electrical and mechanical properties of the film. The electrical and mechanical properties of the steady-state surface layer may be expected to change radically with changing experimental conditions. For any particular case the ultimate film-determining process is difficult to evaluate.

Since the surface of the anode is rough, with burrs and pits on the surface, the depth of this layer above one point may be considerably different from the depth above another point. The concentration of the reaction product

involving the metallic ion would be higher at the anode surface than in the bulk solution, and since the concentration gradient determines the rate of movement, the thickness of the film is critical: the gradient above a burr would be higher than the gradient above a pit. Hence the current through a burr would be greater than the current through a pit: metal would be removed faster from above a burr than from above a pit, and a smoothed surface would result.

That the thickness of the layer is of critical importance can easily be shown. The probability that the surface of a real film is not planar but rather follows the general contour of the surface does not affect the argument. In Fig. 1 two

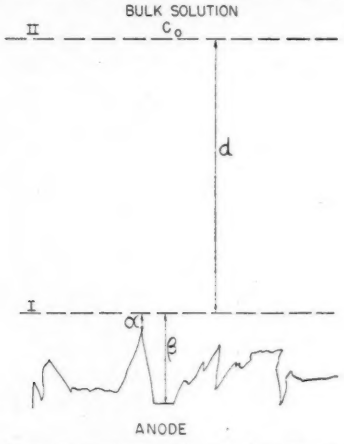


FIG. 1. Imaginary rough anode surface with two imaginary and arbitrary thicknesses of the film.

imaginary thicknesses of layer are indicated. When the steady state in the process has been reached, a uniform concentration of metal ions, c, would be expected to exist at the metal-layer interface, no matter what the contour, while the concentration, c_0, in the bulk solution would be uniform. In the case of a thin film (I), the concentration gradient above a burr, $(dc/dx)_b$, is given, in approximation, by $(c-c_0)/\alpha$, while the concentration gradient above a pit, $(dc/dx)_p$, is $(c-c_0)\beta$. Because $\beta \gg \alpha$ $(dc/dx)_b \gg (dc/dx)_p$; and, assuming the same small area of anode, $i_b \gg i_p$.

In the case of a thick film (II), however, $d \gg \alpha$ or β. Then $(dc/dx)_b = (c-c_0)/(\alpha + d)$, and $(dc/dx)_p = (c-c_0)/(\beta + d)$; and since α and β are both small with respect to d, $(dc/dx)_b \approx (dc/dx)_p$, or $i_b \approx i_p$.

For anodic electrolytic polishing, then, it is necessary that physical, chemical, and electrochemical conditions be such that there is established and maintained during current flow a surface layer (1) whose resistivity to ion or molecular movement approaches some optimum value: a resistivity higher than that of the bulk solution, yet low enough to permit passage of ions and water molecules and to discourage oxygen liberation; (2) whose thickness approaches some optimum value such that $i_b \gg i_p$.

Strong basic solutions should be ideal for electropolishing those amphoteric metals whose oxides or hydroxides are not too difficultly soluble in strong solutions. Above some minimum apparent current density the concentration of metal ions, X^{n+}, liberated into the anode surface layer would become high enough to supersaturate the anode layer with respect to the gelatinous $X(OH)_n$. This $X(OH)_n$ is dissolved by the alkali metal hydroxide, MOH, to give the zincate ion, aluminate ion, etc., XO_n^{n-}. Stoichiometrically, the process may be expressed:

$$X^{n+} + nMOH \rightarrow X(OH)_n + nM^+$$

$$\text{and } X(OH)_n + nMOH \rightarrow nM^+ + XO_n^{n-} + nH_2O.$$

However, there is indication that at least in some cases the primary product of the process is the oxide, subsequent conversion to the hydroxide taking place if the hydroxide is more stable (6). In such cases the rate of conversion from a tight oxide film to the more loose gelatinous hydroxide would be expected to be governed by the rates of the diffusion processes through the film, as already discussed.

Those amphoteric metals which form at practical current densities viscous, permeable, gelatinous oxide or hydroxide films when anodized in basic solutions would be expected to be electropolished with ease. Metals whose oxides or hydroxides are difficultly or only slowly soluble and form tight, impermeable, highly resistive layers on the surface would be expected to be impossible to electropolish in basic solution.

EXPERIMENTAL

Samples of several of the amphoteric metals (14), including zinc, aluminum, tin, bismuth, antimony, and lead, were made the anode under a wide range of conditions of caustic concentration, apparent anode current density, temperature, and time. Preparation of the surfaces was standardized in order that relative times of anodization would have a meaning. The metal specimens were filed, and then mechanically polished to a fine, but rough, surface with emery paper. The specimens, 2.5 cm. × 1.2 cm. × 0.16 cm., were mounted midway between parallel platinum plates, 2.5 cm. × 2.5 cm., connected together externally. The specimens were half submerged, so that the anodes were actually 1.2 cm. × 1.2 cm. Four temperatures, 0°, 25°, 53°, and 90° C., and six concentrations of aqueous potassium hydroxide, 1 *N*, 5.36 *N*, 8 *N*, 12 *N*, and 19 *N*, and 25 *N*, were used to scan for possible electropolishing conditions.

Aluminum and Zinc

These gave brilliantly electropolished surfaces over a wide range of experimental conditions. Since aluminum oxide and hydroxide are easily soluble in potassium hydroxide, 5.36 *N* potassium hydroxide proved to be too concentrated to permit formation of an anodic film at reasonable current densities; the aluminum was simply electrolytically stripped from the surface leaving the macrocrystalline structure of the aluminum visible. However, in 1 *N* potassium hydroxide, treatment at a current density of 0.1 amp. $cm.^{-2}$ for 30 min., for instance, produced a brilliantly electropolished surface. Zinc is treated in detail below.

Antimony

A polished luster could not be obtained on antimony. However, with difficulty, under extended treatment at a current density of 0.02 amp. cm.$^{-2}$ for 30 min. in 5.36 *N* potassium hydroxide, deburring of a rough surface could be obtained. Under these conditions the finish was smooth but rather dull.

Lead

Lead behaved similarly to antimony. A brightly electropolished surface could not be obtained, although the dull surface of oxided lead seemed to be deburred. Formation of heavy dark films during the process was noted, but, although these were fairly easily removed in most cases, the underlying surface remained dull grayish.

Bismuth

Anodic current under various conditions produced no electropolished bismuth surface. The oxide produced on the surface is apparently electrically highly resistive, yet brittle and not bound tightly enough to the bismuth surface, for the anodization is accompanied by intermittent, explosive liberation of oxygen. During these explosions on the surface, pieces of the yellowish oxide film are broken off and the current surges by a factor of 10. The oxide(s) formed on the surface are soluble in hot concentrated potassium hydroxide, but electropolishing of bismuth could not be obtained in a reasonable length of time even under these conditions. Presumably the rate of dissolution of the oxides is slow.

Tin

Kerr (11) has shown that in basic solutions: (1) anodization of tin at 20° C. produces a dark brown film, regardless of conditions; analyses showed the film to contain 81% stannic oxide, 9% stannous oxide, and 10% water, the film, thick and dense; (2) anodization at 50° produces a yellowish film, 68.5% stannic oxide, 12.5% stannous oxide, and 19% water, thin and unstable. Under the first condition tin was found to be electroetched, as in the case of aluminum. That is, after the film has been removed from the surface, the bright, polycrystalline structure (formed by multiple nucleation during solidification from the molten state) of the ingot tin is visible. The dark film is only loosely bound to the surface, and the film falls off in pieces during treatment. This, perhaps, is at least partially responsible for the slight pitting in an otherwise bright and deburred surface. No satisfactory brilliantly electropolished surface could be obtained in 0.1 *N*, 5.36 *N*, or 19 *N* potassium hydroxide from 1 ma. cm.$^{-2}$ to 0.1 amp. cm.$^{-2}$ at 25° C.

Zinc

The conditions for electropolishing zinc were determined in detail in potassium hydroxide solutions over a wide range of concentration, current density, and time, at 0°, 25°, and 53° C.; and then less completely in sodium hydroxide solutions and lithium hydroxide solutions for comparison. The zinc used was of purity 99.99%, obtained from Consolidated Mining and Smelting Co., Trail, B.C.

Three different surface conditions were observed after anodic treatment of zinc in alkaline solution.

(1) At very low current densities there was little or no liberation of gas at either electrode. The surface of the zinc seemed to have undergone little change, and the metal was either unpolished or very slightly polished.

(2) In that range of current densities which proved favorable for good polishing, a thick black deposit was formed on the zinc.* There was little or no oxygen liberated at the anode although hydrogen liberation at the cathode was quite heavy. At the end of an anodic treatment this black layer was removed by either of two methods. The more satisfactory manner consisted of increasing the current through the cell for a fraction of a second, and then cutting it off. After two or three such cycles, the bursts of oxygen gas had caused the layer to lift off the surface, fall to the bottom of the cell, and subsequently to dissolve. This method was satisfactory for both thick and thin films. Alternatively, washing in warm, distilled water or dilute basic solution served to remove the thicker and more loosely bound films, but the washing technique was not very effective for the removal of some very thin and tightly bound films. At fairly high current densities, the rate of removal of metal is very high, and the time necessary for formation of the film and polishing is very short. Some oxygen evolution was noticeable at the higher current densities. Although the thick, black deposit was not maintained under these conditions, mild oxygen evolution apparently did not seriously affect the critical part of the anode layer, for polishing could be obtained under such conditions.

(3) At very high current densities gassing was violent, no film could be maintained, and the surfaces became electroetched. That is, the metal had simply been stripped off, leaving visible the bright polycrystalline surface, as noticed in the case of tin and aluminum. The anodization in this case was accompanied by vigorous stirring due to considerable oxygen evolution.

In Fig. 2 are shown electropolishing templates for zinc in various concentrations of potassium hydroxide at 53° C. It can be seen that with decreasing concentrations of potassium hydroxide the range of time and current density suitable for electropolishing collapses inward and upward. The boundary at high current density represents the current density above which an electroetched surface, instead of an electropolished surface, is obtained. The curved boundary between polished and unpolished zinc is not a critical dividing line, but is a rather diffuse boundary across which the zinc surface must pass as it is being electropolished. At any chosen current density, for example, it has been verified by experiment that as time of anodic treatment increases the zinc surface passes through such qualitatively descriptive phases as "not electropolished", "slightly electropolished", "electropolished", and "brilliantly

* *Recently it was demonstrated by Hoar and Farthing (5) by an amalgamation technique, that even in orthophosphoric acid – water electrolyte a "solid" anodic film is a necessary condition for electropolishing of copper and α-brass: that electroetching or random stripping of the metal from the surface to reveal the underlying structure takes place when conditions are such that no solid film is present. The nature of solid film in this case is not known with certainty, but indications are that it may not be an oxide (1).*

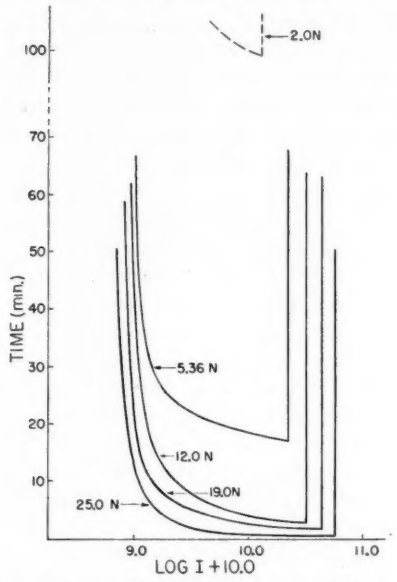
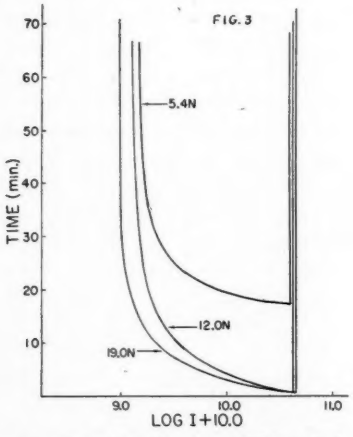


FIG. 2. Templates for the electrolytic polishing of zinc at 53.0° in different concentrations of potassium hydroxide. Each curve outlines the region of time and apparent current density within which zinc can be polished.

electropolished". Although the boundary is diffuse, the curve through the quality "electropolished" is quite definite and is easily reproduced once the standard for the degrees of polish has been set up. The photomicrographs in Fig. 7 serve to indicate the types of surfaces produced. Note that even a fairly well polished specimen, although apparently continuous and smooth to the



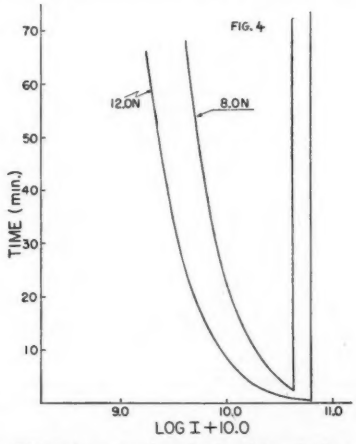


FIG. 3. Templates for the polishing of zinc at 25° C. in potassium hydroxide solutions.
FIG. 4. Templates for the polishing of zinc at 0° C. in potassium hydroxide solutions.

naked eye, is covered with very small pits and craters on and slightly underneath the surface (Fig. 7(*c*)). Electron reflection patterns of these surfaces were those of zinc oxide, and from these the thickness of the zinc oxide film was estimated to be between 40 and 200Å. These polished surfaces have tarnished only slightly after one year in the corrosive fumes of the laboratory.

Fig. 3 shows the range of conditions for electropolishing at 25° C. in potassium hydroxide solutions, and Fig. 4 shows how the range has been reduced by reducing the temperature to 0° C. Fig. 5 shows the boundaries for electropolishing zinc in sodium hydroxide solutions at 25° C., and Fig. 6 for lithium hydroxide at one concentration for comparison.

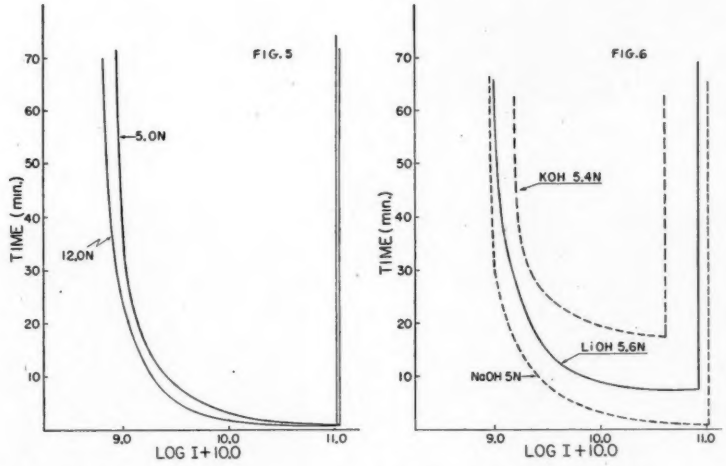


FIG. 5. Templates for the polishing of zinc at 25° C. in sodium hydroxide solutions.
FIG. 6. Template for the polishing of zinc at 25° C. in 5.6 *N* lithium hydroxide solution, with corresponding templates for potassium hydroxide and lithium hydroxide added for comparison.

In each case, that part of the electropolishing range best suited for the production of brilliantly electropolished surfaces is that toward high current density and short time of current flow. The terminal voltage of the electrodes is not presented, as in another case (12), since it is the resistive component of the anodic polarizations which determines the quality of the anodized surface. Hence the terminal voltage may be misleading since it depends critically on certain properties not directly concerned with the electropolishing process, for instance: (1) the thermodynamic, open circuit potential of anode and cathode—these are essentially foreign ion half-cells, capable of considerable variation in e.m.f., (2) true concentration polarizations at both anode and cathode, (3) any hydrogen or oxygen overvoltages, (4) the resistance of the solution between the electrodes.

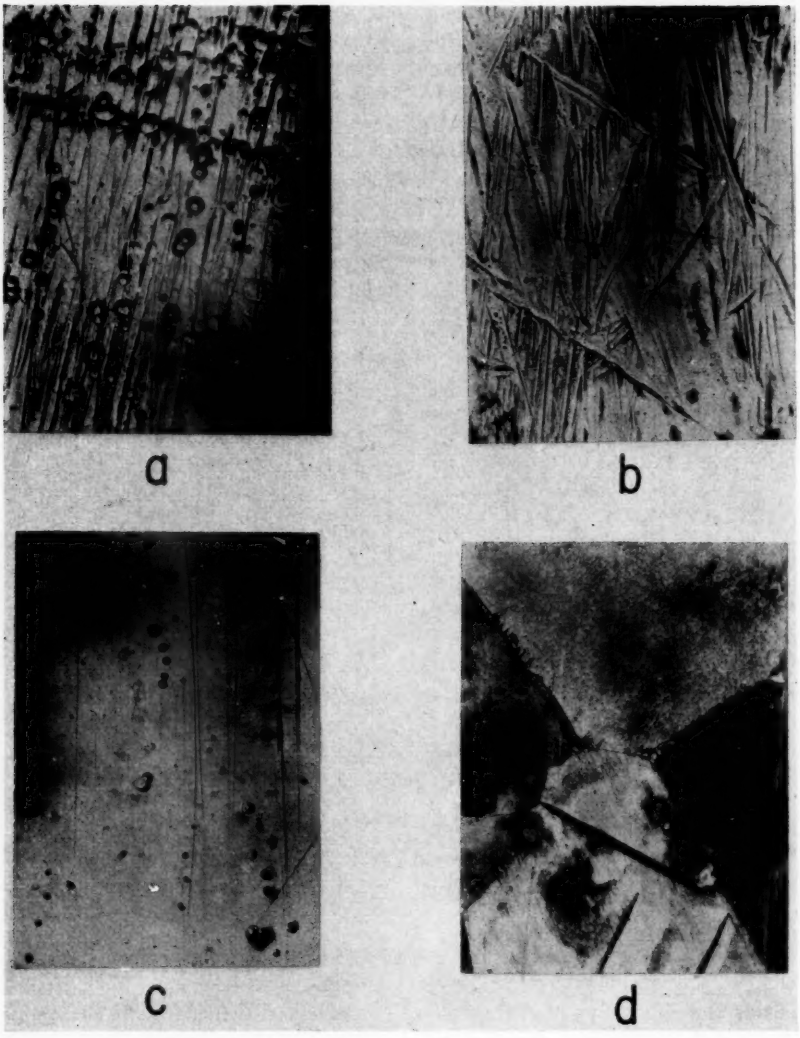


FIG. 7. Photomicrographs (approx. × 250) of surfaces given anodic treatment (*a*) not polished, (*b*) partially deburred and slightly electropolished, (*c*) well polished, (*d*) electroetched.

ANALYSIS AND DISCUSSION

General Trends

Concentration Effect

Experimentally it was found that at any chosen current density the polishing is done more efficiently at higher concentrations of OH^-. A consideration of the process involved indicates that at low concentrations the rate of solution

of the film is probably slower than at high concentration, and one might expect that the film could grow thicker. As discussed above, the thicker the film, the less efficient it is for electropolishing. At higher concentrations of potassium hydroxide the film would be expected to be removed faster, and thus at the same current density the film is probably thin and more efficient for electropolishing.

Current Density Effect

Below some fairly critical current density in each case, electropolished surfaces could not be obtained, presumably because the rate of solution of the surface film was greater than its rate of production; that is, no film effective for electropolishing was formed. Of course, it is very probable that even at very low current densities, a very tight film, Angstroms thick, exists, following closely the surface contour, but this film would be too thin to be effective for polishing. Above some critical high current density, the anode concentration polarization becomes so high that the potential of decomposition of water of OH^- is exceeded and oxygen is liberated. This causes violent stirring in the vicinity of the electrode, the film is broken mechanically as well as is dissolved, and the result is an electroetch—even removal of metal from each part of the surface.

Temperature Effect

Increased temperature was found to widen the electropolishing range of current density and time, as is noticed in Figs. 1, 2, and 3. Higher temperature, as well as increased concentration of OH^-, would be expected to increase the rate of solution of the film, keep the film thin, and thus permit electropolishing to be carried out in less time. It is noticed (Fig. 3) that at the lowest temperature not only was the range found to be considerably more narrow than at 25° and 53° but also that electropolishing could be effected in only the most concentrated solutions available at that temperature. No polishing at all was obtained in the 5.4 *N* potassium hydroxide at 0° C. That is, the rate of solution of the film is so slow at 0° C. that only in the most concentrated solution is the film kept thin and mechanically loose enough to be effective.

Cation Effect

The range of electropolishing conditions in sodium hydroxide is considerably larger than in the same concentration of potassium hydroxide (Fig. 5), and the range in lithium hydroxide falls in between the ranges in sodium hydroxide and potassium hydroxide. This is shown in Fig. 6. Differences must be attributed to differences in the properties of Li^+, Na^+, and K^+ since the weighed equivalent concentrations of OH^- are all the same. The fact that zinc electropolishes in much less time in 5 *N* sodium hydroxide than in 5 *N* potassium hydroxide at the same current density is interpreted as resulting from a thinner and more efficient film being formed in sodium hydroxide than in potassium hydroxide. The anodic film formed in lithium hydroxide is apparently less efficient than that formed in sodium hydroxide, but is more efficient than the anodic film formed in potassium hydroxide of the same concentration, at the same current density and temperature. Hence the rate of removal of

the film formed in sodium hydroxide must be greater than that of the film formed in lithium hydroxide, and this in turn must be greater than the rate of removal of the film formed in potassium hydroxide. Since the removal of the surface film is probably by means of the chemical process,

$$Zn(OH)_2 + 2\ MOH \rightarrow M_2ZnO_2 + 2H_2O,$$

the rate of removal of the film might be controlled by (1) the diffusion of MOH toward the anode, the diffusion of M_2ZnO_2, in whatever form, away from the anode into the solution, or the diffusion of water or MOH through the film; or (2) the chemical reaction of the dissolution process. In terms of Fick's law and rate theories (4), the rate of diffusion of MOH into, or reaction products away from, the film–solution interface depends upon the concentration gradient between the interface and the bulk solution, upon molecular or ionic size and weight, the nature and extent of hydration, and upon molecular and ionic cross-bonding or association in the solution. The rate of the chemical process would depend upon the activity of MOH at the interface and upon the exact composition of the film, strength of molecular and ionic association, and cross-linking in the film. The rate of diffusion of water, or MOH through the film depends on the concentration gradients and on the tightness of binding in the film itself. In each case the rate would depend upon those factors which determine the activation free energy for the process.

That the rate of diffusion of MOH into the interface from the bulk solution probably does not determine the thickness of the film is indicated by the fact that diffusion coefficients for the 1 *N* MOH in aqueous solution (figures for higher concentrations are not available) in order of decreasing value are KOH > NaOH > LiOH (7), and the mobilities of the cations decrease in the same order, $K^+ > Na^+ > Li^+$(15). Thus the effects noted above, namely the efficiency of electropolishing in NaOH > LiOH > KOH, must be attributed to (1) diffusion of M_2ZnO_2, in some form, away from the anode, or the diffusion of MOH or water through the film, or (2) the differences between the rates of the chemical reactions of dissolution of zinc hydroxide in sodium hydroxide, potassium hydroxide, and lithium hydroxide.

Detailed Analysis

A kinetic analysis of the data for zinc in potassium hydroxide solutions establishes some apparent trends and provides further information on the processes involved. For this purpose let us define a "percentage electropolished" to replace the qualitative descriptions, and let 100% electropolished be the equivalent of the qualitative term "electropolished" used above. "Slightly electropolished" would be translated into < 100 percentage units. Since each of the curves in Figs. 2, 3, 4, and 5 refers to the quality "electropolished", each point on the curves refers to a surface of quality 100 E.P.U. Hence, if 100 E.P.U. is achieved in time t, then the average rate at which the surface is being polished is [100 (E.P.U.)]/t; or average rate = (100/t) E.P.U./minute. That the definition and use of such a term as average rate is justified is seen when one considers that once the steady state in the anodic process has been established—and this takes only seconds in this case—

further radical changes in the characteristics of the surface film would not be expected.

Table I shows average rates of polishing at different current densities,

TABLE I

I, amp. cm.$^{-2}$	Temp., ° C.	Concentration of KOH, normality	t_{100} E.P.U., min.	Rate of polishing, E.P.U./min.
0.18	53.0	5.36	25.5	3.9 ± 0.3
		12.0	12.6	7.9 ± 1.0
		19.0	7.5	13. ± 2.
		25.0	4.0	25. ± 3.
	25.0	5.4	34.0	3.0 ± 0.5
		12.0	20.5	4.9 ± 0.6
		19.0	11.5	8.7 ± 0.7
	0.0	8.0	$\gg$100	$\ll$1.0
		12.0	65	1.6 ± 0.3
0.32	53.0	5.36	22.0	4.5 ± 0.3
		12.0	8.0	12.5 ± 1.5
		19.0	5.0	20. ± 3.
		25.0	1.8	55. ± 10.
	25.0	5.4	25.0	4.0 ± 0.3
		12.0	10.5	9.5 ± 1.0
		19.0	7.5	13. ± 1.0
	0.0	8.0	~100	~1.0
		12.0	35	2.9 ± 0.3
1.0	53.0	2.0	~100	~1.0
		5.36	18	5.6 ± 0.5
		12.0	4.0	25. ± 6.
		19.0	2.0	50. ± 10.
		25.0	0.9	110. ± 25.
	25.0	5.4	19.7	5.1 ± 0.5
		12.0	4.3	23. ± 5.
		19.0	3.1	32. ± 7.
	0.0	8.0	22.0	4.5 ± 0.4
		12.0	8.0	12.5 ± 1.2

temperatures, and concentrations of potassium hydroxide. Times of anodic treatment and maximum probable errors were taken from the experimental points. Fig. 8 shows the dependence of the average rate of polishing on the concentration of potassium hydroxide. It is seen that at the low current density in concentrations of potassium hydroxide up to about 16 N the rate of polishing appears to be linear; that is, the film-determining process seems to be first order with respect to potassium hydroxide. However, at current density 0.32 amp. cm.$^{-2}$ there are slight indications of curvature even below 16 N. At the high current density (1.0 amp. cm.$^{-2}$) the deviation from linearity is quite definite.

Table II lists average rates, taken from the experimental data, at the three

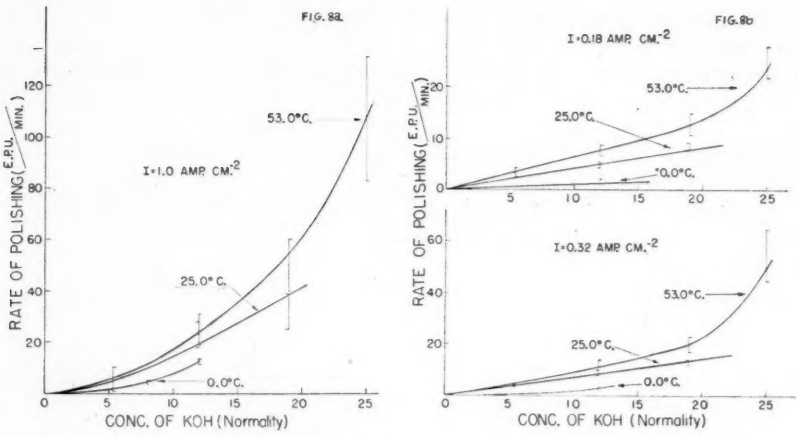


FIG. 8, (*a*) and (*b*). Average rate of polishing vs. concentration of potassium hydroxide for different current densities.

TABLE II

Concentration of KOH, normality	*I*, amp. cm.$^{-2}$	Temp., ° C.	Rate of polishing, E.P.U./min.	log rate	$(1/T) \times 10^3$, ° K.$^{-1}$
12	0.18	0.0	1.6 ± 0.3	0.20 ± 0.08	3.66
		25.0	4.9 ± 0.6	0.69 ± 0.04	3.35
		53.0	7.9 ± 1.0	0.90 ± 0.05	3.07
	0.32	0.0	2.9 ± 0.3	0.46 ± 0.05	3.66
		25.0	9.5 ± 1.0	0.98 ± 0.04	3.35
		53.0	12.5 ± 1.5	1.10 ± 0.05	3.07
	1.0	0.0	12.5 ± 1.0	1.10 ± 0.03	3.66
		25.0	23. ± 5.	1.36 ± 0.09	3.35
		53.0	25. ± 6.	1.40 ± 0.09	3.07
19	0.18	25.0	8.7 ± 0.7	0.94 ± 0.03	3.35
		53.0	13. ± 2.	1.11 ± 0.07	3.07
	0.32	25.0	13. ± 1.	1.11 ± 0.04	3.35
		53.0	20. ± 3.	1.30 ± 0.06	3.07
	1.0	25.0	32. ± 7.	1.51 ± 0.08	3.35
		53.0	50. ± 10.	1.70 ± 0.08	3.07

current densities, in 12 *N* and in 19 *N* potassium hydroxide solution. Arrhenius plots of log rate vs. $1/T$ for these data are shown in Fig. 9. In the Curves *a*, *b*, and *c*, a definite curvature is noted. Tangents to the curves at 0.0° C. and 53.0° C. show the activation energies for the process to decrease with increasing current density and decrease with increasing temperature:

I (amp. cm.$^{-2}$)	E^* (cal./mole)	
	0.0° C.	53.0° C.
0.18	9800	3000
0.32	8100	2200
1.00	4300	1800

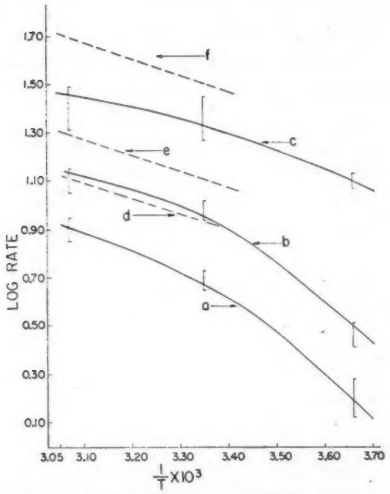


FIG. 9. Arrhenius plots for rate of polishing at various temperatures. *a*, *b*, and *c* 12 *N* potassium hydroxide; *d*, *e*, and *f* 19 *N* potassium hydroxide.

The low values at higher temperature suggest that a liquidlike diffusion process ultimately determines the characteristics of the layer at higher temperatures. The higher values at the lower temperature might refer equally well to the increasing importance of (1) diffusion through a much tighter film at the low temperature, or (2) the rate of the chemical process of dissolution. For the concentration 19 *N* the activation energies were taken from data for 25° and 53° only, since the poor solubility of potassium hydroxide at 0° C. makes the experiment impossible. However, the values were seen to be all about 3200 cal./mole, indicating that even at these higher concentrations the characteristics of the film are controlled by some physical process, probably diffusion.

This temperature and concentration information has suggested the following picture of the anodic processes of film formation and maintenance:

(1) At the low current densities the activation energies for the polishing process show that the heavy black deposit noted on the surface must be very tight at 0° C., much more porous at 53° C. Since the film is tight, penetration of the film is probably quite slow. Since the concentration of free potassium hydroxide in the film in this case would be expected to be quite

small, dissolution of the film must take place mostly at the film–solution interface, and loosening of the film due to internal dissolution by potassium hydroxide must be negligible. Thus, the rate of polishing would be expected to be linear with respect to potassium hydroxide concentration below that concentration at which internal dissolution of the film becomes important. This is verified by the data of Fig. 8*b*. Indications are that at low current densities the rate of polishing is ultimately controlled by diffusion of the potassium hydroxide through the film toward the anode for precipitation of the fresh zinc ions. That is, the film is built up at the anode–film interface and removed mostly at the film–solution interface.

(2) At higher current densities, when the continuous destroying and rebuilding of the surface layer is much more rapid, the concentration of the potassium hydroxide in the film becomes increasingly important. The rate of penetration of potassium hydroxide to any point in the film, expressed by Fick's law, is proportional to the product of the concentration gradient and the diffusion coefficient. When the higher concentrations of potassium hydroxide are present in the film, internal dissolution of the film becomes appreciable, and the strength of binding in the film decreases. Thus, both the concentration gradient and the diffusion coefficient are increasing functions of the potassium hydroxide concentration. Therefore, since the binding in the film ultimately depends upon the concentration of potassium hydroxide in the film, the rate of supply of potassium hydroxide (and hence the rate of polishing) must depend upon some power of potassium hydroxide concentration greater than unity. That this is so is shown especially in the higher current density curves of Fig. 8: the rate deviates from linear dependence on potassium hydroxide concentration toward the parabolic, although the activation energies for the process under these conditions are still about 3200 cal./mole. At the higher current densities some oxygen was liberated, and the stirring so obtained probably aided the supply of potassium hydroxide to the interface and provided some additional mechanical loosening of the film.

(3) At the very high current densities the film was broken mechanically by the oxygen bubbles, no film could exist, and an electroetch was the result.

It is suggested from this interpretation of the results that the primary function of the film is to provide a loose, though tenuous, structure through which the passage of reaction products is by diffusion alone, convection and small eddy currents in the immediate vicinity of the anode having been minimized or eliminated.

Other General Considerations

The results on aluminum and zinc indicate that there probably exists for each temperature an optimum range of concentration of electrolyte for anodic polishing. Thus the work on zinc has shown that at any temperature there is a minimum concentration below which electropolishing is not feasible because of the necessarily extended lengths of time of anodic treatment. The work on aluminum indicates that aluminum hydroxide dissolves so fast in 5 *N* potassium hydroxide solution that the film is not formed at all at reasonable

current densities, but that in lower concentrations of potassium hydroxide removal of the film is slower, and the film grows to a thickness which permits efficient electropolishing. Hence, a minimum concentration of potassium hydroxide for efficient electropolishing was found for zinc, and a maximum concentration for efficient electropolishing was found for aluminum.

In those cases in which electropolishing could not be obtained, viz. bismuth and tin, and antimony and lead only partially, a combination of effects is probably responsible. The oxides of lead and antimony immediately on the surface seem thin, and too tightly bound to be easily removed in the potassium hydroxide solutions used, and no polishing was obtained even though a second heavier film was formed above that immediately on the surface. The tin oxide is brittle, probably because of strong cross-bonding within the film and slow penetration of water and potassium hydroxide. The rate of solution of the film would be slower, the film thick, very highly resistive, and inefficient for electropolishing. Hence the concentration range for electropolishing tin is apparently toward higher concentrations of potassium hydroxide, beyond the limits of solubility of potassium hydroxide.

SUMMARY AND CONCLUSIONS

Thus a kinetic analysis of data on the electrolytic polishing of zinc in alkali hydroxide solutions has established some trends and generalizations which seem to fit a proposed qualitative theory of the anodic processes taking place during the electrolytic polishing of metals. An anodic surface layer is pictured whose electrical and mechanical properties vary radically with metal, electrolyte, concentration of electrolyte, current density through the anode, temperature, and time of anodic treatment. The electrical and mechanical properties of the film determine the nature of the resulting surface. The experimental results are interpreted in terms of the theory, and the interpretation permits a rather detailed description of the anodic processes occurring in the film.

This condition of the surface after the metal has been made the anode of an electrochemical cell offers an additional fact relating to the polarizations of the anode. In any such experiment this fact is "measured" automatically, and, if interpreted in terms of the qualitative ideas presented herein, provides considerable useful additional information concerning the nature of the anodic processes involved. Some success has already been achieved along this line during work on another problem.

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DEPENDENCE OF MOLECULAR PROPERTIES OF CONJUGATED COMPOUNDS ON THE STATE OF ELECTRONIC EXCITATION[1]

By C. Sándorfy

ABSTRACT

Reasons are given for the belief that many new chemical reactions may be obtained in the excited electronic states of the molecules. By the examples of nitrobenzene, *trans* → *cis* isomerization of stilbene and azobenzene, by an interpretation of experimental results concerning acidity and basicity of certain bodies in the excited states, and the evaluation of the charges and dipole moments of the C = N group in different excited states, it is shown how the chemical and physicochemical properties of the molecule may vary from one state to another.

INTRODUCTION

Every molecule, in addition to its ground state, possesses a series of quantized excited states, into which it may pass by absorption of a photon.

The majority of photochemical reactions studied to date involve ions or free radicals.

We do not intend to concern ourselves with such reactions here. Instead, we wish to present arguments showing that these reactions constitute only a special case of possible reactions, involving the excited states of the molecules.

From work in theoretical chemistry published in recent years, we know that chemical reactivity is associated with the distribution of the electrons in the molecules. In particular, the case of molecules containing a conjugated system of π electrons has been studied in great detail.

Now, any method of quantum chemistry shows the distribution of the electrons to be different in the different states.

The establishment of this fact presents the possibility of making the molecules participate in reactions in which they would not take part in their ground level or of increasing the speed of reactions that do take place.

It follows that if some convenient way were found of making the molecules react in their excited states, a scarcely exploited field would be opened to chemistry. To accomplish this it would only be necessary to keep a large number of molecules in their excited states during a reaction by the use of a sufficiently intense radiation. A favorable case would be the excitation to states which have a very long lifetime. This is the case for forbidden transitions, especially where a molecule is excited to its first triplet level. Lewis and Kasha have insisted on the importance of the phosphorescence spectra from this point of view (12, 13, 15).

REACTIONS IN THE EXCITED STATES

Daudel and Pullman (7) appear to have been the first to evaluate a molecular diagram which describes the charge distribution in an excited state for a conjugated molecule. They did this for cyclopentadiene. Crawford and

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Coulson (4) then took up the dimerization of acenaphthylene under the influence of light, and Sándorfy (20) studied the photooxidation and photodimerization of the acenes.

We do not intend to discuss these examples further here.

Chemical reactivity, as it appears in theoretical chemistry, depends on a fairly large number of factors: the charge, the bond order, the free valence number, the "autopolarizability" (3), the activation energy, and the stability of the end products (see for example (8)). For the excited states, their evaluation presents some difficulties.

We shall try here to present some examples in which one of these quantities appears to be of preponderant importance, thus making the study of the problem easier.

However, we shall not confine ourselves to the problems of chemical reactivity. It is clear that other physicochemical properties may vary from one state to another along with the distribution of the electrons.

(A) *Modification of the Orienting Effect of Substituents*

It is well known that, in the case of benzene, substituents exercise a certain orienting effect with respect to a second substitution. For example, the nitro-group orients a second electrophilic substituent in the meta position (during a nitration, for example), and this is explained by the fact that in meta position the positive charge is smallest and repels least the attacking group, which is a positive ion.

It is not possible to obtain ortho- or paradinitrobenzene by direct nitration in any appreciable amount.

Would it be possible to do this by means of a reaction carried out under the influence of light?

Fernandez (9) has evaluated the molecular diagrams of the first three excited states of nitrobenzene by a refined LCAO treatment.

These three levels lie close to one another and will probably be excited simultaneously, if a light source emitting continuous radiation is employed (about 4500–3500 Å in this particular case).

On examining the three corresponding diagrams we note that everywhere the meta position ceases to be the most favored one with respect to an electrophilic reagent (Fig. 1– effective charges given in electron units).

It can therefore be predicted that the formation of ortho- or paradinitrobenzene in appreciable quantities would be possible in the excited states.

Rumpf (19) has studied the possibility of verifying these predictions experimentally.

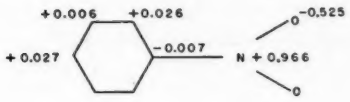
(B) *Photoisomerization*

The bond order (3) appears to be the most important quantity in the case which we are now going to discuss.

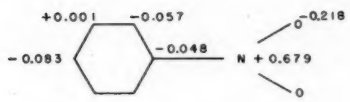
We are concerned with *trans* → *cis* isomerization due to the effect of light (also *cis* → *trans*, although more rarely).

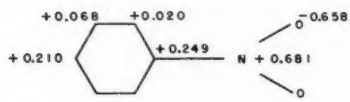
Smakula and Wassermann (22, 23) studied the problem in connection with the absorption spectrum of stilbene, and they came to the conclusion that in

GROUND STATE



EXCITED STATES





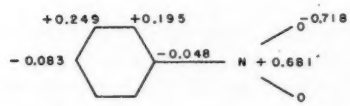


FIG. 1

order to obtain isomerization it was not necessary to remove the π component of the ethylenic bond, but only to excite the electrons in this bond. Later Lewis, Magel, and Lipkin (16) again took up the problem.

Smakula thought that the transition must be due to the electrons of the ethylenic bond. To-day we know that such a localization is not admissible, in principle, in a conjugated system. It is necessary to study the levels of the π electrons of stilbene. This has been done for the fundamental state by Buu-Hoï, Coulson, P. and R. Daudel, Martin, and A. and B. Pullman (1). We have evaluated the bond orders of the first allowed excited level (2). Here are the results:

GROUND STATE

EXCITED STATE

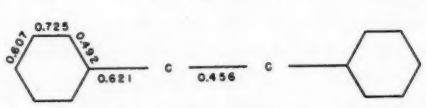


FIG. 2

It is noted at once that there is a large decrease in the bond order of the ethylenic bond ($\Delta p = 0.384$).

For azobenzene the case is quite similar.

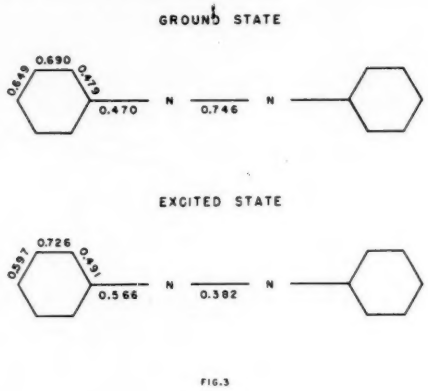


FIG. 3

Here $\Delta p = 0.364$.

All this suggests that in the excited state, in conformity with Smakula's idea, the bond about which an isomerization occurs, although it remains a "double bond", becomes less "double". It can be imagined, therefore, that a rotation will occur more easily about it in the excited state than in the fundamental state.

Mulliken and Roothaan (17) and Parr and Crawford (18) carried out calculations on the variation of the energy of the ethylene molecule, on twisting the plane of one CH_2 group relative to that of the other about the C = C axis for various electronic states, and obtained results in satisfactory agreement with experiment.

(C) *Modification of Electrolytic Dissociation Constants*

The tendency of an acid such as phenol to lose a proton is greatest when there is a high positive charge on the oxygen, and the concentration of the protons in the medium is low.

On the other hand a base such as aniline will attract a proton and liberate an hydroxyl ion all the more easily when the negative charge on the nitrogen is great (or its positive charge small), and the concentration of the protons in the medium is high (see for instance (24)) (provided other things, such as changes in resonance energy, are equal).

Förster drew attention to the fact that if the acid or base absorbs a photon and passes into an excited state, the distribution of the charges is profoundly altered, and consequently the acidity or basicity is likewise altered (10).

In order to demonstrate this phenomenon, he studied the absorption spectra and fluorescence spectra of certain acids and bases, in which the pH of the medium varied from 0 to 14. The absorption spectra depend on the state of dissociation of the ground level, the fluorescence spectra on that of the excited level.

We intend to follow up these experiments with some theoretical calculations. We shall evaluate the charges due to the π electrons in all cases by the usual method of molecular orbitals, and we shall take into account the charges due to polarization of the σ electrons by means of the charge effect method (5, 14) of Daudel.

We shall consider aniline and phenol as models for the study of larger molecules on which these phenomena were observed.

In the case of aniline, the nitrogen carries a charge equal to -0.13 electron in the ground level. (The Coulomb integral is $\alpha_N = 0.61$.) It will be understood, therefore, that even in a solution of low acidity it will be able to attract a proton (Fig. 4*a*).

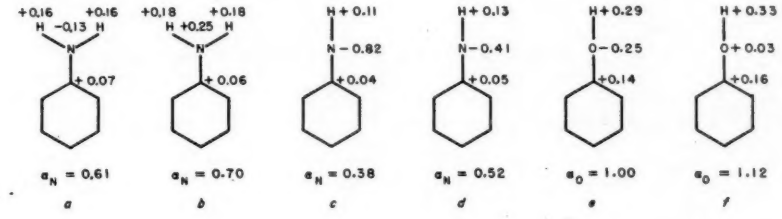


FIG. 4.

Thus the conjugation between the benzene nucleus and the nitrogen is reduced and instead of the aniline absorption spectrum (first band at 2860 Å) only the "benzenic" spectrum (2550 Å) will be found (see 11).

The greater the number of aniline molecules which acquire a third proton, the more intense the "benzenic" band will become at the expense of the "anilinic", and this number will depend on the pH. The "anilinic" band will disappear entirely if the solution is sufficiently acid.

It is a case of the intensity of one band increasing while that of another decreases; there is no question of a band being displaced towards shorter or longer waves.

We have taken the mean value of the charges appearing on the first two close-lying excited levels, and we have found $+0.25$ on the nitrogen (Fig. 4*b*).

This is a considerable modification. Simply by absorbing a photon the aniline becomes much less basic. Since it has a positive charge it will tend to repulse protons. Consequently, the "anilinic" band will disappear at a much more acid pH value in fluorescence than in absorption.

According to Förster (10), in a very basic solution the hydroxyl ions of the solution may separate a proton from the amino group. The remainder of the molecule, in the ground and excited levels, will have the diagrams in Figs. 4*c* and 4*d*. In the ground level, even if this second proton is lost, the molecule will readily acquire another proton because of the high negative charge of the nitrogen.

Therefore we may expect that this form will appear rather in the excited state (i.e., in fluorescence) where the positive charge of the nitrogen in

$C_6H_5NH_2$ is higher, and where once the second proton is lost its negative charge is lower.

The corresponding band will be located at longer wave lengths owing to the decreased electronegative character of the nitrogen.

For phenol, the diagrams of Figs. 4*e* and 4*f* are obtained.

The proton, indeed, can be separated more easily when the molecule is at the excited level. The corresponding band will appear at longer wave lengths in fluorescence at a less basic pH value.

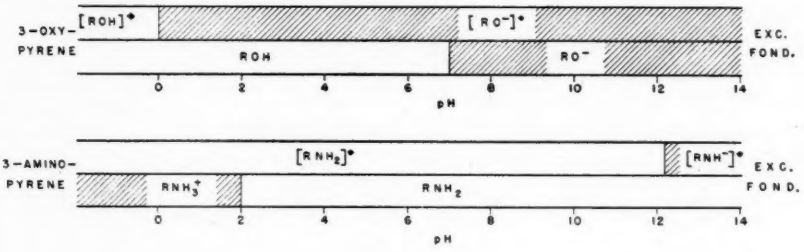


FIG. 5.

The experimental results (10) obtained in the case of 3-amino and 3-oxypyrene, summarized in Fig. 5 (taken from Ref. 10), are quite similar to those which would be expected for aniline and phenol according to our calculations.

Experiments on the α and β naphthols and on the α and β naphthylamines lead to similar observations (10).

We evaluated the molecular diagrams of the α and β naphthols by the method of molecular orbitals, taking $\alpha_O = 1$ for the Coulomb integral of oxygen and $\alpha_c = 0.1$ for the carbon to which it is linked.

We present them here for the ground states and for the first excited states (Fig. 6). The most important fact which may be observed is again the considerable increase of the positive charge on the oxygen due to excitation, and certain important reversals of the values of the charges on other atoms which should not fail to have their effect on the chemical reactivity. We quickly discover atoms, for example, which constitute preferred places for the attack of an electrophilic reagent in the ground level, and which will be preferred places for the nucleophilic reagents in the excited states. Fig. 6 shows also the diagram for the charges of the second excited state of β naphthol.

It is interesting to see that the increase of the positive charge is not as great here as for the first excited state, and that the charges of the two carbons next to the one bound to the oxygen are completely reversed compared with those of the first excited state.

From this it may be predicted that it is quite possible to find higher excited states, in which the change in chemical reactivity, relative to that of the ground level, is not as great as for a lower excited state, and it is even possible that the reactivities of certain atoms of a molecule are of an entirely different character for different excited states.

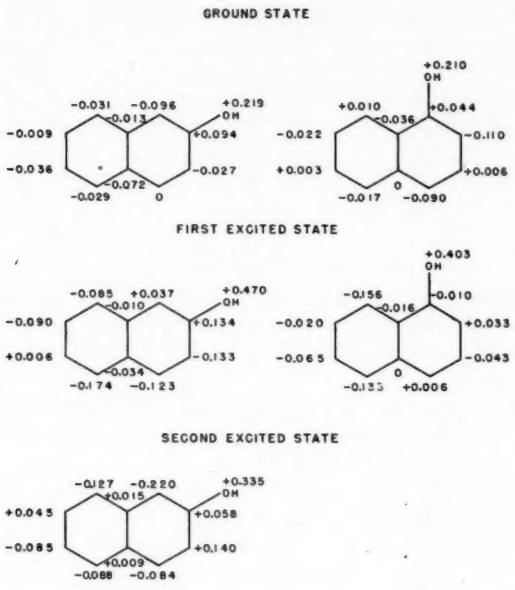


FIG. 6

(D) *Modification of the Polar Moments*

With the aid of definitions recently proposed by Daudel and Laforgue (6) it is possible to evaluate the charges on the atoms, taking into account configurational interaction.

This has been done for the imaginary group C = N (choosing $\alpha_N = 0.5$ as the supplementary Coulomb integral of nitrogen (21)*).

These are the charges for the three states N, V, and Z:

Excitation energies	Charges
N	−0.01 +0.01 C ——— N
$N \rightarrow V$ 11.56 ev. V	−0.52 +0.52 C ——— N
$N \rightarrow Z$ 15.86 ev. Z	+0.51 −0.51 C ——— N

The extent to which conditions may vary from one state to another is clearly evident. Owing to the effect of a photon which takes this group from the N state to the V state the carbon will become very open to attack by an electrophilic reagent, but if, by means of a photon of higher energy, the group is made to pass to the Z state it will become easily attacked by the nucleophilic

* *Certain numerical results have been changed from the values given in (21) owing to a different choice of an integral.*

reagents. All this may be interesting from the point of view of Schiff's bases, $C_6H_5-CH=N-C_6H_5$, for example, where an electronic transition affecting principally the CH = N group (19) probably will be found.

The part of the dipole moment due to the π electrons also varies widely according to the state.

N	$-0.06\ D$
V	$-3.16\ D$
Z	$3.08\ D$

CONCLUSIONS

These few examples seem to point to the fact that the chemical and physicochemical properties of the molecules, in general, must vary in quite an important way depending on the state of energy in which the molecules find themselves.

A more detailed study of the chemical and physicochemical properties of the molecules by both theoretical and experimental methods in their excited states would therefore be very desirable.

There will no doubt be serious technical difficulties to overcome before such experiments can be carried out.

However, there is no reason to believe that these are insurmountable, and, in the event of success, the theory will have opened up a new field to experimentation.

ACKNOWLEDGMENTS

I wish to thank Dr. R. Daudel and Dr. P. Rumpf for many valuable discussions. It is hoped that the experiments undertaken by the latter will confirm the theoretical predictions set forth in the present paper.

The manuscript of this article was completed during my tenure of a National Research Council of Canada Postdoctorate Fellowship.

I wish to acknowledge my gratitude to Dr. R. N. Jones for the interest he has shown in this work, to Dr. D. W. Davidson for assistance in the preparation of the manuscript, and to Mr. D. A. Sinclair for the English translation.

RÉSUMÉ

On donne des raisons de penser qu'un grand nombre de réactions chimiques nouvelles pourraient être réalisées aux états excités des molécules. On montre par les exemples du nitrobenzène, de l'isomerisation *trans* → *cis* du stilbène et de l'azobenzène, par une interprétation des résultats expérimentaux concernant l'acidité et la basicité de certains corps à l'état excité et l'évaluation des charges et des moments dipolaires du groupe C = N à ces différents états, comment les propriétés chimiques et physico-chimiques des molécules peuvent varier d'un état d'energie à un autre.

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BETATRON IRRADIATION OF WATER SATURATED WITH BENZENE[1]

By G. R. Freeman, A. B. Van Cleave, and J. W. T. Spinks

ABSTRACT

The oxidation of benzene to phenol in dilute aqueous solution by Co^{60} gamma rays and betatron X-rays (23 Mev. peak energy) is compared with the oxidation of Fe^{++} to Fe^{+++} under similar conditions. The ratio $\frac{\text{yield of phenol}}{\text{yield of } Fe^{++} \text{ oxidized}}$ was the same for Co^{60} and betatron radiations. The yield for the Co^{60} radiations was about 10% greater than the apparent yield for the betatron radiations, the difference probably being attributable to dose determination at high energies (> 1 Mev.). It is concluded that both reactions are independent of energy and dose rate over the ranges investigated.

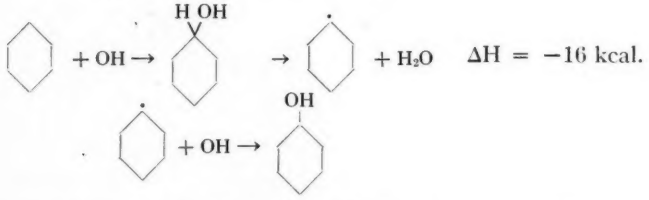
INTRODUCTION

It has been found that when a saturated aqueous solution of benzene is irradiated with X- or γ-rays, phenol, hydrogen, biphenyl, and terphenyl are formed (9, 10). When an n-γ-ray source was used to irradiate the solutions, catechol and products originating from the opening of the benzene ring were produced in addition to those listed above. These products (catechol, etc.) are presumably due to the higher free radical concentration caused by the recoil protons (from neutrons hitting hydrogen atoms) (9).

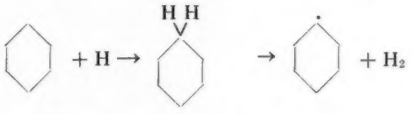
Similar products are obtained by the irradiation of dilute aqueous solutions of sodium benzoate (9, 10).

The latest mechanism (10) advanced for the hydroxylation of benzene on irradiation of its aqueous solution with X-rays is:

$$H_2O \rightsquigarrow H + OH$$

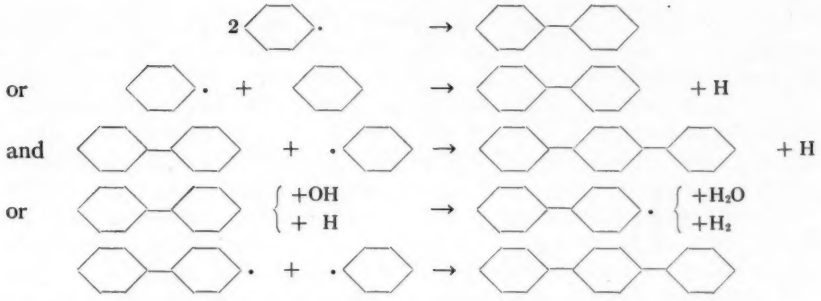


Phenyl radicals may also be formed to a small extent by the reaction:



The phenyl radicals also react to form di- and terphenyl:

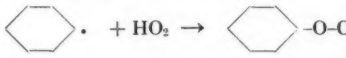
[1] *Manuscript received December 1, 1952.*
Contribution from the Department of Chemistry, University of Saskatchewan, Saskatoon, Sask.



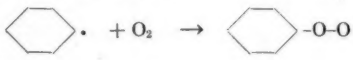
When oxygen is present in the solution, HO_2, formed by the reaction

$$H + O_2 \rightarrow HO_2,$$

is also capable of hydroxylating benzene (10, 3),



This may eventually result in the formation of phenol. Similarly, oxygen may react with the phenyl free radical (3),



which may eventually form phenol.

The yield of phenol in aerated solution is five times as great as the yield in deaerated solution (10).

The yield of phenol is not critically dependent on pH, concentration, temperature, or wave length of incident radiation (10, 3). The yield increases slightly at high (> 10) and low (< 4) pH and decreases by 20% for a 10-fold dilution of the saturated solution (10).

In aerated saturated aqueous benzene solution, the yield of phenol varies directly with the dose up to about 60 kiloroentgens (depending on the amount of oxygen present in the solution and probably also on the dose rate, since oxygen diffuses into the solution from the air above it), beyond which there is a sharp drop in yield, due to the virtual absence of oxygen (10, 3).

The purpose of the present experiments was to carry out the irradiation of aerated saturated aqueous benzene solutions with γ-rays from Co^{60} and with 23 Mev. peak energy X-rays from a betatron. Parallel experiments were carried out on the oxidation of ferrous sulphate solutions so that the ratio of the yield of phenol produced to the yield of Fe^{++} oxidized could be compared for the two different energy sources.

MATERIALS

The water used in the benzene solutions and in all analytical reagents used in phenol analyses was prepared by distilling tap water once from alkaline potassium permanganate in an all-Pyrex still.

The water used in the ferrous sulphate solution and in all analytical reagents

concerned with iron analyses was prepared by distilling tap water once from alkaline potassium permanganate and then once from alkaline manganous hydroxide suspensions (each time in an all-Pyrex still).

The Pyrex test tubes, and ground glass stoppers, used to contain the solutions during irradiation were cleaned with hot chromic acid cleaning solution, rinsed at least three times with tap water, and then at least three times with water distilled from alkaline potassium permanganate.

The benzene used was thiophene-free reagent grade, further purified by shaking once with an equal volume of concentrated sulphuric acid (two minutes) and seven times with equal volumes of distilled water (one minute each time).

The phenol used in the preparation of the standard curve was purified by vacuum distillation from zinc dust.

The Folin-Denis phenol reagent and the standard phenol solution were prepared as in *Colorimetric Methods of Analysis*, Vol. 2, by F. D. Snell. However, it was found that in the phenol standardization, only 10 cc. of normal iodine were necessary to precipitate the triiodophenol (50 cc. of normal iodine solution are prescribed in Snell).

The sulphuric acid used was purified by distilling from potassium dichromate.

EXPERIMENTAL PROCEDURES

Determination of Phenol

Standard phenol solution (0.1 ml.) (5.63 gm./l.) was diluted to 5 ml. with water, and 3 ml. Folin-Denis reagent was added. After thorough mixing, 15 ml. 20% sodium carbonate solution was added, and the blue color was allowed to develop for 20 min. A transmittance curve was then run on the solution in a model DU Beckman spectrophotometer. Maximum absorption occurs at $\lambda = 750$ mμ (see Fig. 1.)

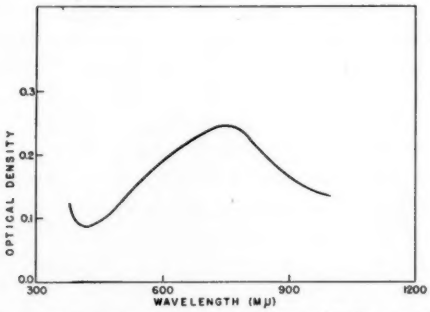


FIG. 1. Transmittance curve for phenol-Folin complex.

The phenol standard curve was obtained by treating solutions of various phenol concentrations (made by diluting standard solution) with Folin reagent and sodium carbonate solution and reading the optical density after 20–25 min. ($\lambda = 750$ mμ, slit 0.015 mm.) using a water blank. The solutions obeyed the

Beer-Lambert Law, and the extinction coefficient was 12,256 l./mole/cm. Optical density is defined by the equation: $D = kcd = (-\log_{10}(T/100))$, where D = optical density, k = extinction coefficient, c = concentration of sample in solutions, d = light path length of cell; T = % transmission (1).

To determine the amount of phenol produced, 1 ml. Folin reagent was added to the irradiated solution, and after thorough mixing, 5 ml. 20% sodium carbonate solution was added. These amounts were used because larger amounts sometimes produced a turbidity. The optical density was read 20–25 min. after the addition of the sodium carbonate. The color was found to be stable for at least one hour after sodium carbonate addition. The irradiated solution did not appear to change its phenol content if allowed to stand 23 hr., after irradiation, before analysis.

Determination of Fe^{++}

The *o*-phenanthroline, sodium citrate colorimetric method was used (7). The irradiated solution was shaken with 5 ml. of 0.1% *o*-phenanthroline, 1 ml. saturated sodium citrate solution was added, and the optical density read in the model DU Beckman spectrophotometer at $\lambda = 510$ mμ, using a water blank.

It was found that the citrate and/or *o*-phenanthroline complexes of Fe^{+++} ion also absorb light at $\lambda = 510$ mμ. Although the absorption is small compared to that of the Fe^{++} ion complex, it must be corrected for in the irradiated solution. The absorption for the Fe^{+++} complexes is plotted in Fig. 2.

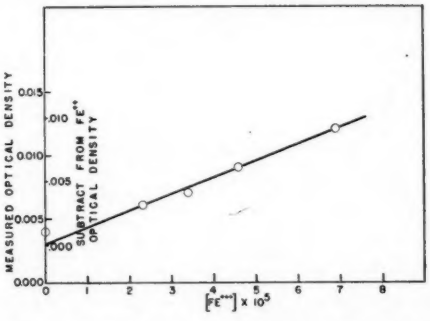


FIG. 2. Fe^{+++}-citrate – *o*-phenanthroline calibration curve.

The standard ferric ion solution used in preparing the curve was made by dissolving ferric ammonium sulphate in 0.8 *N* sulphuric acid. Various concentrations of Fe^{+++} were obtained by diluting this standard solution with 0.8 *N* sulphuric acid.

The optical density of the solution containing everything but iron was about 0.003. This was constant for all solutions measured, and since the μm./l. of Fe^{++} oxidized was measured by subtracting the $[Fe^{++}]$ present in the irradiation solution from the $[Fe^{++}]$ in the original solution, no error was introduced in the final result. However, the ferric ion concentration varied with the dosage, and hence had to be corrected for. This correction was obtained by

subtracting 0.003 from the optical density of the Fe^{+++} complex solution. (The $[Fe^{+++}]$ could be calculated accurately enough from the uncorrected optical densities.) The value thus obtained was subtracted from the optical density of the Fe^{++} solution and the $[Fe^{++}]$ was calculated from the net results. For example, an original Fe^{++} ion solution diluted three times had an optical density of 0.299, corresponding to $[Fe^{++}]$ of 26.0 μm./l. After irradiation the solution, diluted three times, had an optical density of 0.097, corresponding to $[Fe^{++}]$ of 8.4 μm./l. (7). Thus, the approximate $[Fe^{+++}]$ was $26.0 - 8.4 = 17.6$ μm./l. From Fig. 2 this corresponds to an optical density correction of 0.002. Therefore, the corrected optical density of the irradiated solution was $0.097 - 0.002 = 0.095$, corresponding to $[Fe^{++}]$ of 8.1 μm./l. The true $[Fe^{+++}]$ was then $26.0 - 8.1 = 17.9$ μm./l. Taking the dilution factor into consideration, $3 \times 17.9 = 53.7$ μm./l. of Fe^{++} ion were oxidized.

As the oxidation of Fe^{++} ion approaches completion, the correction becomes more significant.

Irradiation with γ-Rays from Co^{60}

Samples (3 ml.) of water saturated with benzene (0.082% at 22° C. (6)) were placed in glass stoppered test tubes in a cylindrical lucite block and irradiated with a 2 curie Co^{60} source (see Fig. 3).

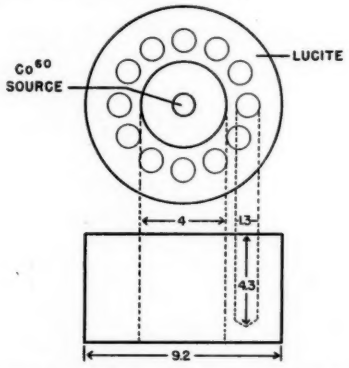


FIG. 3. Lucite block for irradiation with 2 curie Co^{60} source (dimensions in cm.).

Samples (3 ml.) of aqueous ferrous ammonium sulphate solution (0.8 *N* in sulphuric acid) were irradiated in the same way.

The dose rate in roentgens/minute (r./min.) received by each hole in the block was determined using a Victoreen Condenser r.-meter Model 70. The bakelite thimble of a 25 r. chamber was replaced with a lucite one equal in size to the volume of the irradiated solution. It was calibrated against a standard 25 r. chamber using a 1100 curie Co^{60} source. The usual temperature and pressure corrections and the 2% for changing "lucite roentgens" to "air roentgens" at 1.25 Mev. energy must also be applied (7).

Irradiation with X-rays from the Betatron Using 23 Mev. Peak Energy

Samples (2 ml.) of water saturated with benzene, in glass stoppered test

tubes were placed in a cylindrical lucite block which was shielded by cadmium (for details, see Ref. (7)).

Samples (2 ml.) of ferrous ammonium sulphate solution (0.8 *N* in sulphuric acid) were irradiated simultaneously with the benzene solutions.

All samples were placed in the outer ring of holes in the block and the rest of the holes contained test tubes of water. After each sample was removed, a test tube of water was placed in the hole to keep irradiation conditions constant throughout the block.

The dose rate was determined using a 100 r. Victoreen chamber. The Victoreen results were corrected for energy dependence (8% at 23 Mev. peak) and for temperature and pressure (7).

EXPERIMENTAL RESULTS

All results from the irradiation of Fe^{++} and benzene solutions were treated statistically, and the best fitting straight lines were determined using the method of least squares. The yields are listed with their respective probable errors.

Irradiation with Co^{60} γ-Rays

Water Saturated with Benzene

The initial pH of all the benzene solutions was 6.7 (unbuffered). The pH decreased with irradiation to 4.42 at 145 kiloroentgens. This variation is within the pH independent region.

The average temperature was 22.5° C. The dose rate was about 1100 roentgens per hour. The results are plotted in Fig. 4. The average yield of phenol was 2.94 ± 0.08 μmoles/l./kr.

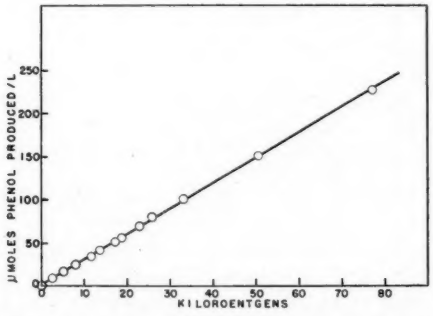


FIG. 4. Irradiation of water, saturated with benzene, with Co^{60} γ-rays.

Ferrous Ammonium Sulphate Solutions (in 0.8 N Sulphuric Acid)

The initial ferrous ion concentration was 7.80×10^{-5} molar. The temperature was 24° C. The dose rate was about 1100 roentgens per hour. The results are plotted in Fig. 5. The average yield of Fe^{++} oxidized to Fe^{+++} by Co^{60} γ-rays was 16.8 ± 0.2 μmoles/l./kr. Complete oxidation of Fe^{++} to Fe^{+++} was observed.

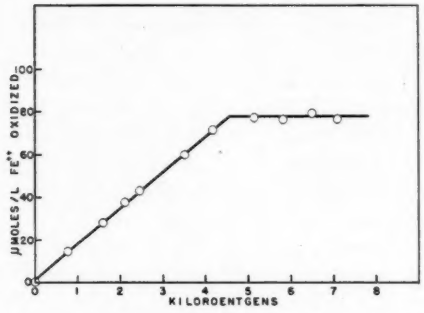


FIG. 5. Irradiation of ferrous sulphate solutions with Co^{60} γ-rays.

Irradiation with Betatron X-rays—23 Mev. Peak Energy

Water Saturated with Benzene

The solutions were exactly similar to those used in the Co^{60} γ-irradiations. The average temperature was 27° C. The dose rate was about 20,000 roentgens per hour. The results are plotted in Fig. 6. The average yield of phenol was 2.64 ± 0.08 μmoles/l./kr.

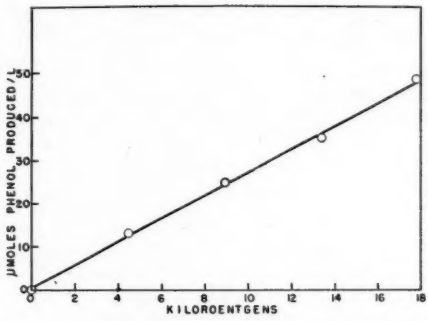


FIG. 6. Irradiation of water, saturated with benzene, with betatron X-rays, 23 Mev. peak energy.

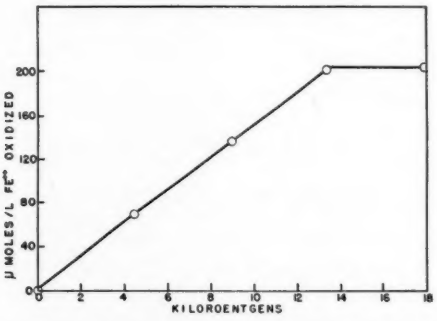


FIG. 7. Irradiation of ferrous sulphate solutions with betatron X-rays, 23 Mev. peak energy.

Ferrous Ammonium Sulphate Solutions (in 0.08 N Sulphuric Acid)

The initial ferrous ion concentration was 2.04×10^{-4} molar. The average temperature was 27° C. The dose rate was about 20,000 roentgens per hour. The results are plotted in Fig. 7. The average yield of Fe^{++} oxidized to Fe^{+++} was 15.0 ± 0.2 μmoles/l./kr. Complete oxidation of Fe^{+++} was observed.

The results are summarized in Table I.

TABLE I

SUMMARY OF RESULTS OBTAINED WITH BENZENE SOLUTIONS AND IRON SOLUTIONS USING Co^{60} γ- AND BETATRON X-RAYS

Radiation source	Solution	Yield	
		(μM./l./kr.)	G(molecules/100 ev.)
Co^{60}—Average energy 1.25 Mev. γ-rays	Benzene	2.94 ± 0.08	3.05 ± 0.08
	Fe^{++}	16.8 ± 0.2	17.4 ± 0.2
Betatron—23 Mev. peak energy X-rays	Benzene	2.64 ± 0.08	2.74 ± 0.08
	Fe^{++}	15.0 ± 0.2	15.6 ± 0.2

Stein and Weiss (10) using 200 kv. X-rays obtained M/N 0.75 for air saturated solutions of benzene.

DISCUSSION

From Table I it is seen that the ratio $\frac{\text{yield of phenol}}{\text{yield of } Fe^{++} \text{ oxidized}}$ for equal doses of Co^{60} γ-rays is 2.94/16.8 = 0.175. The same ratio for betatron X-rays with 23 Mev. peak energy is 2.64/15.0 = 0.176. The difference between these two values is not significant, and it thus appears that the Fe^{++} and benzene solutions behave in the same manner with respect to the particular combined variation in the dose rate and energy of incident radiation in the present experiments. These ratios are independent of Victoreen errors and corrections made in converting "lucite roentgens" to air roentgens, since the only requirement is that the doses be equal. With the Co^{60} source equal doses may be obtained by placing samples in the same geometry for equal periods of time. With the betatron, equal doses may be obtained by irradiating the samples simultaneously in the rotating lucite block used in these experiments.

The actual values of the yields (μM./l./kr.) of phenol, and of Fe^{++} oxidized, by irradiation of aqueous solutions of benzene and ferrous ion, respectively, indicate that there is about a 10% difference in the results obtained from the Co^{60} γ-irradiations and from the betatron X-irradiations at 23 Mev. peak energy. This difference could be due to any one or combination of four factors: (1) Victoreen dose determination at high energy (> 1 Mev.), (2) energy of incident radiation, (3) dose rate, (4) the betatron X-rays are emitted in pulses of about 4μsec. duration and frequency of 180 per second. Thus, the dose rate in each pulse is extremely high, and might enhance the ordinary dose rate effect.

The median energy of the photons from the betatron at 23 Mev. peak is about 9 Mev. (calculated from a theoretical Schiff distribution curve for

maximum photon energy of 23 Mev. which has been modified by absorption of donut, monitor, and lucite). At this high energy, uncertainties in the Victoreen dose determination may account for all or most of the variation; thus, it would appear that both the ferrous and benzene systems are independent of dose rate and energy of incident radiation over the range investigated. This conclusion is supported further by the fact that the ferrous system was found to be independent of dose rate over the range 500–1500 r./hr. by Dewhurst (5) and over the range 72–3600 r./hr. by Miller (8). Since both the benzene and ferrous systems may be regarded as being essentially water, the energy absorbed per roentgen would be the same, i.e., 93 ergs/gm./r.

The fact that the ratios: $\frac{\text{yield phenol}}{\text{yield } Fe^{++} \text{ oxidized}}$ are the same for the Co^{60} and betatron irradiations, probably indicates that the water is the main factor affected, and this effect is relatively independent of the solute. Thus, an indirect reaction mechanism is indicated, and reaction is probably due to activated water molecules or water products such as OH, HO_2, etc., and not due to a direct hit on the solute. Of course, this conclusion holds only for the dilute solutions described above and may not apply to concentrated solutions. The possibility that secondary radiation from water may have an effect should also be mentioned (2, 4).

ACKNOWLEDGMENTS

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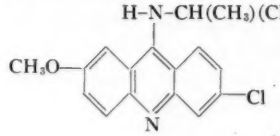
STUDIES IN THE PREPARATION OF ANTIMALARIALS FROM PYRIDINE[1]

By Henry Gilman and John T. Edward[2]

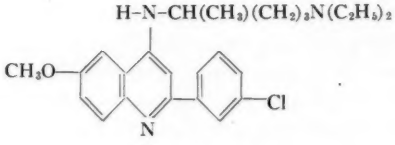
ABSTRACT

The addition of aryllithium compounds to pyridine followed by air oxidation gives satisfactory yields of several 2-arylpyridines. These are readily oxidized by perbenzoic acid to 2-arylpyridine-N-oxides, from which 2-aryl-4- and 6-chloropyridines may be obtained. 2-Arylpyridines and aryllithiums give low yields of 2,6-diarylpyridines. From three different 2-arylpyridines three antimalarials modelled after the plasmoquin type have been prepared.

In earlier investigations in this laboratory (8, 9, 14, 15) it was found that certain "open models" of atebrin (I) such as 2-(3′-chlorophenyl)-4[(α-methyl-δ-diethylaminobutyl)-amino]-6-methoxyquinoline (II) were active against

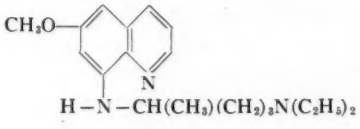


I

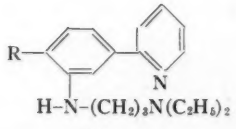


II

experimental avian malarial infections. Consequently, three open models of plasmoquin (III) having the basic side chain on the phenyl group of a 2-phenylpyridine have been prepared. Of these,



III



IV

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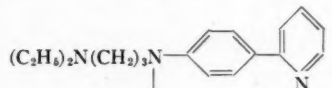


V

2-(3′-[γ-diethylaminopropyl]-amino-4′-methoxyphenyl)-pyridine (IV; R = OCH_3) and 2-(3′-[γ-diethylaminopropyl]-amino-4′-methylphenyl)-pyridine (IV; R = CH_3) proved inactive, while 2-(4′-[γ-diethylaminopropyl]-aminophenyl)-pyridine (V) showed slight activity. Somewhat surprisingly, 2-*p*-tolylpyridine also gave indications of activity. It may be significant that the active compounds are vinylogues of α-picoline and a 2-aminopyridine, in both of which there exists the possibility of a tautomeric shift of hydrogen to the hetero nitrogen atom (19, pp. 32, 91); such a possibility has been suggested in explaining the antimalarial activity of atebrin (23) and other compounds (4).

The general method of synthesis of these plasmoquin models is illustrated by the example below. The aryllithium was prepared in all cases by direct interaction of the appropriate aryl bromide with lithium. It has been observed that *p*-anisyllithium metalates *p*-bromoanisole so that the reaction of the latter with lithium ordinarily yields a mixture of *p*-anisyllithium and 2-methoxy-5-bromophenyllithium (10). However, if the *p*-anisyllithium is prepared very rapidly, the extent of metalation is slight and relatively pure *p*-anisyllithium is obtained.

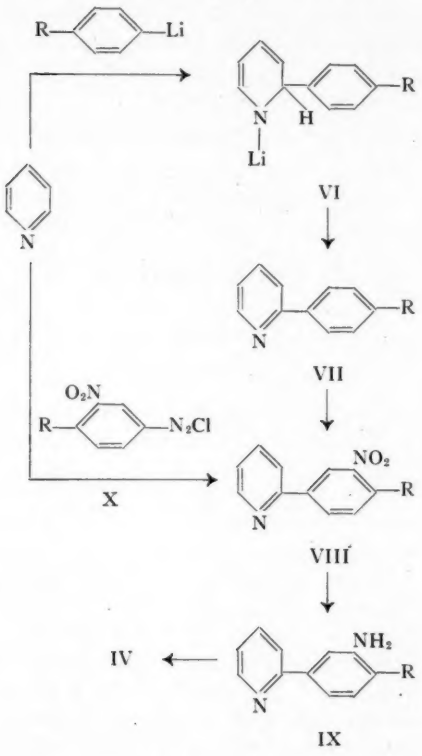
The addition of an aryllithium to pyridine gives an N-lithiodihydropyridine (VI), which hitherto has been converted to the desired 2-arylpyridine (VII) by heating above 100° and splitting out lithium hydride (5, 25, 26, 27). Oxidation of the N-lithiodihydro intermediate with dry air gives, particularly in the cases of 2-*o*-anisyl- and 2-*p*-anisylpyridine, significantly improved yields, though in the case of the *o*-anisyl compound the yield is still low.

Since this work was completed, the preparation of 2-phenylpyridine in 60% yield by oxidation with nitrobenzene of 2-phenyl-1,2-dihydropyridine (produced from (VI; R = H) when the reaction mixture is poured into water) has been reported (7).

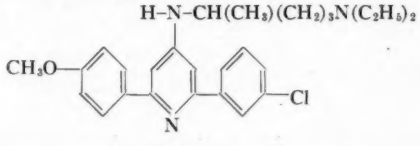
The attempt to prepare 2-phenylpyridine by coupling 2-bromopyridine with phenyllithium gave only a low yield of the desired compound; the isolation of pyridine from the hydrolyzed reaction mixture indicates that a halogen–metal interconversion reaction took place, giving bromobenzene and 2-pyridyllithium. A similar reaction with 3-bromopyridine, using *n*-butyllithium, has been described by Gilman and Spatz (12).

The nitration of 2-phenyl- and 2-*p*-anisylpyridine gave nitro compounds of known orientation (6, 16); however, it was necessary to establish the position of nitration of 2-*p*-tolylpyridine (VII; R = CH_3). This was done by an independent synthesis of the product, 2-(3′-nitro-4′-methylphenyl)-pyridine (VIII; R = CH_3), by the reaction of diazotized 2-nitro-4-aminotoluene (X) with pyridine. This reaction gave, besides (VIII), two other compounds, presumably the isomers formed by substitution at the 3- and 4-positions of pyridine.

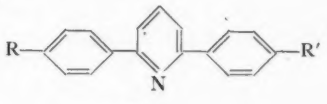
The synthesis of open models of atebrin (e.g. XI) was also envisaged,



through the stages 2,6-diarylpyridine → N-oxide → 4-chloropyridine → 4-(basic alkylamino)-pyridine. However, only low yields of 2,6-diarylpyridines (e.g. XII; R = R′ = H; R = $(CH_3)_2N$, R′ = H; and R = $(CH_3)_2N$, R′ = CH_3) were obtainable from aryllithiums and 2-arylpyridines.



XI



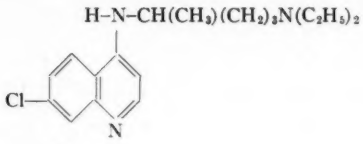
XII

The best yields were obtained by conducting the reaction above 100° and forcing the addition of the aryllithium to the sluggish 2-arylpyridine.

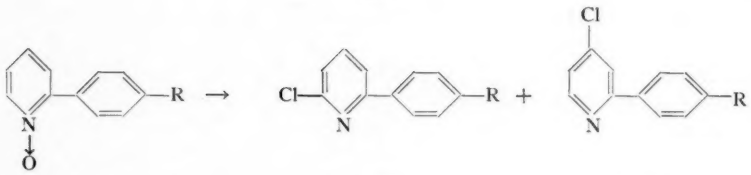
The oxidation of 2,6-diphenylpyridine by a large excess of perbenzoic acid gave a low yield of the N-oxide (cf. 20). On the other hand, 2-phenylpyridine and 2-*p*-anisylpyridine gave good yields of their N-oxides. The introduction of phenyl groups is known to decrease the basicity of the pyridine nucleus (19, p. 71); evidently with two or more of these electron-withdrawing groups

substituted in pyridine the availability of the unshared electron pair of the nitrogen for co-ordination with oxygen is sharply decreased.

The possibility of preparing open models of the highly active 4-(α-methyl-δ-diethylaminobutyl)-amino-7-chloroquinoline (SN 7618) (XIII) was next



XIII



XIV XV XVI

considered. It is known that the N-oxides of pyridine (2), quinoline (1, 20), and similar compounds, on treatment with sulphuryl chloride or phosphorus oxychloride, yield mixtures of the 2- and 4-chloro bases. These may be separated because of the greater basicity of the 4-chloro compounds (e.g. 18). 2-Phenylpyridine-N-oxide (XIV; R = H) and 2-*p*-anisylpyridine-N-oxide (XIV; R = OCH_3) also gave in this way a mixture of chlorinated compounds; the more basic were assumed to be the 4-chloro derivatives (XVI; R = H and OCH_3), and were isolated as picrates; the less basic, which did not form picrates, to be 2-chloro derivatives (XV; R = H and OCH_3). These compounds contain reactive halogen atoms (19, p. 78) which should be easily replaced by the basic side chain to give open models of XIII.

In searching for an alternative synthesis of 2-aryl-6-chloropyridines, 2-chloropyridine was treated with phenyllithium, but no reaction occurred. Evidently the chlorine deactivates the pyridine nucleus (cf. Gilman and Spatz (13)).

EXPERIMENTAL

2-Phenylpyridine

This compound was prepared essentially in accordance with the procedure of Evans and Allen (5), except that the dihydro intermediate was oxidized with air instead of being heated to 110° C. in toluene. Five minutes after addition of slightly more than an equivalent amount of pyridine to phenyllithium, the green color in Gilman's Colour Test I (11), indicative of phenyllithium, had given place to a red color, possibly owing to the dihydro intermediate. The mixture was maintained a further 10 min. under nitrogen, and then dry air was passed over the stirred mixture. The completion of oxidation, indicated when the red color was no longer given, required from 6 to 24 hr.,

depending on the size of the run. Yields, which did not seem to be much affected by varying the temperature of this oxidation between 0° and 35° C., varied from 40% to 57%, about the same as the yields (40–50%) obtained by Evans and Allen.

Reaction of Phenyllithium with 2-Bromopyridine

Phenyllithium (0.065 mole) in 50 cc. of ether was added dropwise over two hours to a stirred solution of 10.2 gm. (0.065 mole) of 2-bromopyridine in 50 cc. of ether. After hydrolysis, the ether layer gave on distillation 3.5 gm. of a yellow liquid boiling at 35–50° C. (20 mm.), which consisted of a water-insoluble liquid and of pyridine, identified by the formation of its picrate (m.p. and mixed m.p.); and 0.5 gm. (5% of theory) of 2-phenylpyridine, b.p. 80° (0.5 mm.), forming a picrate, m.p. 173° to 174° C. (25).

2-(p-[γ-Diethylaminopropyl]-aminophenyl)-pyridine (V)

2-Phenylpyridine was nitrated by a solution of potassium nitrate in sulphuric acid, and the mixture of 2-*m*- and 2-*p*-nitrophenylpyridine separated by the procedure of Forsyth and Pyman (6). Reduction of 2-*p*-nitrophenylpyridine to 2-*p*-aminophenylpyridine was accomplished either with tin and hydrochloric acid (6), or by dissolving in 10 parts of ethanol and heating on the steam bath for seven hours with 10 parts of a saturated aqueous sodium sulphide solution (64% yield). 2-*p*-Aminophenylpyridine (4.1 gm.; 0.024 mole) was heated with 6.7 gm. (0.036 mole) of γ-diethylaminopropyl chloride hydrochloride to 130° C. for four hours, and to 190° C. for 12 hr. The brown glassy melt which formed was dissolved in dilute hydrochloric acid. When the solution was made alkaline a brown oil separated, which was taken up in ether, dried, and distilled. The 2-(*p*-[γ-diethylaminopropyl]-aminophenyl)-pyridine was obtained as a viscous yellow oil, b.p. 185–190° C. (1 mm.), n_D^{25} 1.6166, d_{25}^{25} 1.0482; observed molar refraction R_D (from the Lorenz-Lorentz equation), 94.55. Calc. (from constants of Vogel (24)) 89.35*. The yield was 5.1 gm. or 68%. Calc. for $C_{18}H_{25}N_3$: N, 14.83%. Found: N, 14.90%.

The compound gave with picric acid a red oil which could not be crystallized.

2-m-Aminophenylpyridine

Seven grams of 2-*m*-nitrophenylpyridine dissolved in 70 cc. of ethanol was heated for seven hours on a steam bath with 70 cc. of aqueous saturated sodium sulphide solution. The solution was filtered from a small amount of colored material and diluted with water. The red oil which separated was taken up in benzene, and the extract dried and distilled. Three grams (50% yield) of yellow oil, b.p. 145–147° C. (0.1 mm.), which crystallized on standing to a solid melting at 72–73° C., was obtained. Calc. for $C_{11}H_{10}N_2$: N, 16.48%. Found: N, 16.38%.

Since the completion of this work, this compound has been described by Cook, Heilbron, and Reed (3) who report a m.p. of 72–74° C.

* *The exaltation of molar refraction noted here and in later examples occurs when the pyridine ring is attached to an aromatic nucleus; when it is attached to alkyl groups, the difference between the observed and calculated molar refractions is less than 1%.*

The *picrate*, crystallized from ethanol, melted at 219–220° C. Calc. for $C_{17}H_{13}O_7N_5$: N, 17.54%. Found: N, 17.70%.

p-Anisyllithium

This compound was prepared from the reaction of 18.7 gm. of *p*-bromoanisole with 1.9 gm. of lithium following the conventional techniques, except that the time of addition of *p*-bromoanisole was reduced to 12 min. and the total time of the reaction to 17 min. This was achieved by having the lithium in very small pieces about 0.5 mm. in thickness, and by cooling the reaction flask with ice water once refluxing of ether had commenced. Carbonation with solid carbon dioxide gave anisic acid melting at 175–184° C. (using a Fisher-Johns heated metal block). Pure anisic acid melted at 185° C.; the admixture of 10% of 2-methoxy-5-bromobenzoic acid lowered the m.p. to 150° C. Hence the m.p. of the carbonation product indicated that it contained probably less than 5% of 2-methoxy-5-bromobenzoic acid.

2-p-Anisylpyridine (*VII; R = OCH_3*)

The addition of *p*-anisyllithium to pyridine, followed by air oxidation of the dihydro intermediate, gave an oily solid boiling at 120–135° C. (0.1 mm.). This was crystallized from petroleum ether to give a 35% yield of 2-*p*-anisylpyridine, melting at 47–50° C.; its picrate melted at 189° C. and did not depress the m.p. of an authentic specimen prepared by the method of Haworth, Heilbron, and Hey (16). These authors report a m.p. for the base of 50–51° C. and a m.p. for the picrate of 191–192° C. Their b.p. (160–190° C. at 0.1 mm.) is about 40° higher than ours.

When 2-*p*-anisylpyridine was prepared by the method of Evans and Allen (5), a smaller yield of a more impure product was obtained, which gave on repeated recrystallization from ligroin a 6% yield of base melting at 46–49° C.

2-o-Anisylpyridine

Addition of *o*-anisyllithium to pyridine was very slow, and even after refluxing the ethereal solution for eight hours Colour Test I gave a faint green color. (Gilman and Spatz (14) found the addition of *o*-anisyllithium to quinoline less complete than the addition of other aryllithiums.) The mixture was then air oxidized and worked up in the usual way to give an 18% yield of yellow oil boiling at 120–140° C. (0.1 mm.), which formed a picrate melting at 152–155° C. Haworth, Heilbron, and Hey (16) report a m.p. for the picrate of 155–156° C.; again their b.p. (160–190° C. at 0.1 mm.) appears to be about 40° too high.

When *o*-anisyllithium was allowed to react with pyridine and the reaction mixture then treated according to the procedure of Evans and Allen, no 2-*o*-anisylpyridine was formed. The fraction of the product boiling at 120–140° C. (0.1 mm.), treated with picric acid, gave an unidentified yellow picrate, m.p. 167–175° C., and considerable amounts of tar; none of the other fractions gave any crystalline derivative with picric acid.

2-(3'-Amino-4'-methoxyphenyl)-pyridine (*IX; R = OCH_3*)

2-*p*-Anisylpyridine, nitrated in accordance with the procedure of Haworth,

Heilbron, and Hey (16), gave 2-(3′-nitro-4′-methoxyphenyl)-pyridine (VIII; R = OCH_3). This material was then reduced with aqueous sodium sulphide solution in the same way as 2-*m*-nitrophenylpyridine. After removal of most of the ethanol by distillation, a 95% yield of 2-(3′-amino-4′-methoxyphenyl)-pyridine crystallized out. The crude material melted at 92–94° C.; recrystallization from methanol–water gave pale tan needles melting at 94–95° C. Calc. for $C_{12}H_{12}ON_2$: N, 14.00%. Found: N, 14.25%. The *picrate*, crystallized from methanol, melted at 219–220° C. Calc. for $C_{18}H_{16}O_8N_5$: N, 16.32%. Found: N, 16.29%.

2-(3′-[γ-Diethylaminopropyl]-amino-4′-methoxyphenyl)-pyridine (IV; R = OCH_3)

Six grams (0.030 mole) of 2-(3′-amino-4′-methoxyphenyl)-pyridine and 8.4 gm. (0.045 mole) of γ-diethylaminopropyl chloride hydrochloride were heated together at 150° C. for nine hours. The glassy melt was worked up in the manner described above for V. A heavy yellow oil, reddening slowly on contact with air, and almost setting to a glass at room temperature, was obtained; b.p. 195–200° C. (0.5 mm.), n_D^{25} 1.5859. The yield was 4.3 gm. (46%). Calc. for $C_{19}H_{27}ON_3$: N, 13.42%. Found: N, 13.65%. No crystalline picrate could be formed.

2-p-Tolylpyridine (VII; R = CH_3)

This compound was prepared in 62% yield by the action of *p*-tolyllithium on pyridine, using the air oxidation method as described for 2-phenylpyridine. It was a yellow oil, b.p. 93–98° C. (1 mm.), d_{25}^{25} 1.055, n_D^{25} 1.6107. R_D observed 55.66, calc. 53.02. Calc. for $C_{12}H_{11}N$: N, 8.28%. Found: N, 8.14%.

The picrate melted at 181–182° C. Calc. for $C_{18}H_{14}O_7N_4$: N, 14.07%. Found: N, 14.28%.

2-(3′-Nitro-4′-methylphenyl)-pyridine (VIII; R = CH_3)

A. *By the Nitration of 2-p-Tolylpyridine*

To a stirred solution of 42 gm. (0.25 mole) of 2-*p*-tolylpyridine in 35 cc. of sulphuric acid, cooled by an ice bath, was added dropwise a solution of 25 gm. (0.25 mole) of potassium nitrate in 100 cc. of sulphuric acid. The mixture was stirred for 10 min. at room temperature, and for 30 min. at 100° C. It was cooled, poured on ice, and neutralized with ammonium hydroxide. The brown flocculent precipitate, on crystallization from methanol, gave 38.9 gm. (73%) of brownish needles, melting at 58–61° C. and a second crop of 3.5 gm. (6.5%), m.p. 55–59° C. Recrystallization from methanol, after decoloration with Norit, gave white needles, m.p. 60–61° C. Calc. for $C_{12}H_{10}O_2N_2$: N, 13.09%. Found: N, 13.40%. The *picrate* crystallized from methanol in small, yellow prisms, m.p. 184–184.5° C. Calc. for $C_{18}H_{13}O_9N_5$: N, 15.80%. Found: N, 16.24%.

B. *By the Action of Diazotized 2-Nitro-4-aminotoluene (X; R = CH_3) on Pyridine*

2-Nitro-4-aminotoluene (7.6 gm.; 0.05 mole), prepared by a modification of the procedure of Nölting and Collin (21), was dissolved in 25 cc. (0.25 mole) of concentrated hydrochloric acid and 12 cc. of water, and diazotized by

3.4 gm. (0.05 mole) of sodium nitrite in 10 cc. of water. The solution of diazotized amine was then added dropwise with stirring to 100 cc. (1.24 mole) of pyridine, over a period of 45 min. A mildly exothermic reaction maintained the temperature at 40–45° C. The reaction mixture was stirred for 30 min. while being heated on a steam bath, and then worked up by the methods employed in similar reactions by Haworth, Heilbron, and Hey (16). Three grams of a yellow oil boiling at 155–160° C. (0.1 mm.) was obtained. This was treated with picric acid in methanol, and the yellow solid obtained was subjected to systematic fractional crystallization from acetone and from ethanol to yield three different picrates. The least soluble, m.p. 217–219° C., crystallized from ethanol–acetone (4: 1) in lemon-yellow, woolly tufts of fine needles, and was probably the picrate of *4-(3'-nitro-4'-methylphenyl)-pyridine*. Calc. for $C_{18}H_{13}O_9N_5$; N, 15.80%. Found: N, 15.65%.

The more soluble fraction was separated into a small amount of a yellow solid, m.p. 240–250° C., probably the impure picrate of 3-(3'-nitro-4'-methylphenyl)-pyridine, and hard canary-yellow prisms melting at 183–185° C., which were shown by mixed m.p. to be identical with the picrate of the *2-(3'-nitro-4'-methylphenyl)-pyridine* prepared by the nitration of 2-*p*-tolylpyridine.

2-(3'-Amino-4'-methylphenyl)-pyridine (*IX; R = CH₃*)

Reduction of the nitro compound with sodium sulphide was accomplished in the same manner as the reduction of 2-*m*-nitrophenylpyridine. A yield of 88.5% of long yellowish needles, m.p. 109–110° C., was obtained. Recrystallization from methanol failed to raise the melting point. Calc. for $C_{12}H_{12}N_2$: N, 15.22%. Found: N, 15.43%. The *picrate* crystallized from methanol in tufts of needles, m.p. 186–187° C. Calc. for $C_{12}H_{15}O_7N_5$: N, 16.95%. Found: N, 17.10%.

2-(3'-[γ-Diethylaminopropyl]-amino-4'-methylphenyl)-pyridine (*IV; R = CH₃*)

2-(3'-Amino-4'-methylphenyl)-pyridine (4.5 gm.; 0.024 mole) and 6.9 gm. (0.037 mole) of γ-diethylaminopropyl chloride hydrochloride were fused together at 160° C. for four hours, and the glassy melt was worked up in the same way as for V. A yellow oil was obtained, b.p. 185–190° C. (0.5 mm.), d_{25}^{25} 1.0272, n_D^{25} 1.5887, R_D observed 97.54, calc. 94.00, weighing 4.6 gm. (63% yield). Calc. for $C_{19}H_{27}N_3$: N, 14.14%. Found: N, 14.38%. No crystalline picrate could be formed.

2,6-Diphenylpyridine (*XII; R = R' = H*)

When 2-phenylpyridine was allowed to react with an equivalent amount of phenyllithium in ethereal solution at 35° C. under nitrogen, addition was still incomplete after 80 min., as shown by a pale blue color given by the reaction mixture in Colour Test I. Air oxidation and working up in the usual manner gave a large recovery of 2-phenylpyridine, boiling at 85–90° C. (0.1 mm.), and identified by forming the picrate melting at 174° C. (25), and some 2,6-diphenylpyridine distilling at 195–200° C. (1 mm.). Crystallization of the latter from petroleum ether gave a 13.5% yield of solid melting at 79–81° C.; by repeated recrystallization from ethanol the melting point was raised to 81° C.;

m.p. of picrate 169° C. Scholtz (22) reports the same melting points for the base and picrate.

On attempting to force addition of phenyllithium to 2-phenylpyridine by refluxing the mixture in ether–toluene at 60° C. under nitrogen it was found that even after 90 min. Colour Test I was pale blue. The mixture was air oxidized and worked up as before to give a 16% recovery of 2-phenylpyridine (isolated as pure picrate from the fraction boiling at 85–100° C. (0.1 mm.)) and 30% yield of impure 2,6-diphenylpyridine; after one crystallization from methanol the yield was 24%, m.p. 79–81° C.

When 2-phenylpyridine was reacted with phenyllithium and the procedure of Evans and Allen (5) followed, a 34% yield of crude 2,6-diphenylpyridine was obtained, but still about 10% of 2-phenylpyridine was recovered.

2,6-Diphenylpyridine-N-oxide

A 350 cc. chloroform solution of 20 gm. (0.087 mole) of 2,6-diphenylpyridine and 0.176 mole of perbenzoic acid was kept in an ice box for 18 hr., and at room temperature for three days. Titration then showed that only 0.031 mole of perbenzoic acid remained. The chloroform solution was extracted with sodium hydroxide solution and dried over sodium sulphate. Evaporation of the solution at reduced pressure gave a yellow oil. On addition of a small amount of ether–ligroin to the oil, 7 gm. of white crystals, m.p. 80–115° C., separated out; the filtrate on being cooled to −10° C. gave a further 5 gm., m.p. 60–70° C. These crops were extracted twice with ether, which served to remove 2,6-diphenylpyridine, of which 3.3 gm. (16%) was recovered in this manner. The extracted solid melted at 105–123° C.; crystallization twice from chloroform – petroleum ether gave 1.2 gm. (5.6%) of pure 2,6-diphenylpyridine-N-oxide, m.p. 125–126° C.; and a second crop (1.8 gm.; 8.4%) melting at 121–126° C. Calc. for $C_{17}H_{13}ON$: N, 5.67%. Found: N, 5.84%. The *picrate* crystallized from ethanol in yellow prisms, m.p. 161–162° C. Calc. for $C_{25}H_{16}O_8N_4$: N, 11.75%. Found: N, 11.92%.

2-p-Dimethylaminophenylpyridine (*VII*; $R = (CH_3)_2N$)

This compound was prepared from the reaction of *p*-dimethylaminophenyllithium with pyridine essentially in accordance with the procedure of Evans and Allen (5). It distilled as a yellow oil, b.p. 160–162° C. (0.1 mm.), which set to a solid melting at 87–92° C. (63% yield). Repeated recrystallization from ligroin and from aqueous acetone gave white crystals, m.p. 97–98.5° C. Calc. for $C_{13}H_{14}N_2$: N, 14.15%. Found: N, 13.96%. The *picrate* crystallized from acetone in long fibrous orange needles, m.p. 194–195° C. Calc. for $C_{19}H_{27}O_7N_5$: N, 16.39%. Found: N, 16.30%.

2-p-Dimethylaminophenyl-6-phenylpyridine (*XII*; $R = (CH_3)_2N$, $R' = H$)

The reaction of *p*-dimethylaminophenyllithium with slightly more than an equivalent amount of 2-phenylpyridine according to the method of Evans and Allen (5) gave 2-*p*-dimethylamino-6-phenylpyridine, b.p. 230–240° C. (0.1 mm.). After crystallization from benzene and from benzene–methanol, a 13% yield of white needles melting at 172–173° C. was obtained. Calc. for

$C_{19}H_{18}N_2$: N, 10.22%. Found: N, 10.22%. The *picrate* was more soluble in methanol than the free base and separated as fluffy, orange crystals, m.p. 143–144° C., with one molecule of methanol of crystallization. Calc. for $C_{25}H_{21}O_7N_5.CH_4O$: N, 13.09%. Found: N, 12.93, 13.15%.

2-p-Dimethylaminophenyl-6-p-tolylpyridine (*XII; R* = $(CH_3)_2N$, *R'* = CH_3)

The reaction of *p*-tolyllithium with 2-*p*-dimethylaminophenylpyridine, following the procedure of Evans and Allen (5), gave a 23% yield of impure solid, b.p. 257° C. (0.5 mm.). Decolorization in benzene solution with Norit followed by recrystallization from benzene and benzene–methanol gave a 9% yield of white crystals, m.p. 196–197° C. Calc. for $C_{20}H_{20}N_2$: N, 9.72%. Found: N, 9.78%. The *picrate* was more soluble in methanol than the free base. It crystallized as a fluffy, orange solid melting at 157–158° C.

2-Phenylpyridine-N-oxide (*XIV; R* = *H*)

A 350 cc. chloroform solution containing 20 gm. (0.13 mole) of 2-phenylpyridine and 0.167 mole of perbenzoic acid was left in the refrigerator for 40 hr. It was then extracted with sodium hydroxide solution, dried over sodium sulphate, and evaporated down to a volume of 60 cc. On dilution with 50 cc. of petroleum ether and cooling, 10.7 gm. (48% yield) of white needles melting at 153–155° C. separated. Concentration of the mother liquors gave a further 4.2 gm. (19% yield) melting at 145–155° C. Recrystallization from benzene raised the m.p. to 155–155.5° C. Calc. for $C_{11}H_{19}ON$: N, 8.19%. Found: N, 8.4%.

When the mole ratio of perbenzoic acid to base was increased from 1.28 to 1.66, the total yield rose from 67% to 77%.

The *picrate* of 2-phenylpyridine-N-oxide crystallized in yellow prisms from benzene, m.p. 150–152° C. Calc. for $C_{17}H_{12}O_8N_4$: N, 14.00%. Found: N, 13.95%.

Chlorination of 2-Phenylpyridine-N-oxide

2-Phenylpyridine-N-oxide (4.2 gm.; 0.025 mole) protected from moisture and cooled in an ice bath was treated with 46 gm. (0.34 mole) of sulphuryl chloride. The amine oxide dissolved almost immediately. After standing for a few minutes at room temperature, the solution was refluxed gently for five hours. It was then cooled, added to 200 gm. of cracked ice, and made strongly alkaline with ammonia. The oil separating was taken up in ether and treated with alcoholic picric acid to give the picrate of *2-phenyl-4-chloropyridine* (XVI; R = H), m.p. 177–182° C. The yield was 4.5 gm. (43%). Crystallization from methanol gave yellow prisms, m.p. 180–182° C. Calc. for $C_{17}H_{11}O_7N_4Cl$: N, 13.39%. Found: N, 13.73%.

The solvent was removed from the filtrate of the picrate, and the resultant oil treated with 30 cc. of 5% sodium hydroxide solution to remove excess picric acid. It was then taken up in ether and distilled to give 1.7 gm. (35%) of 2-phenyl-6-chloropyridine (XV; R = H), b.p. 124–125° C. (0.1 mm.), m.p. 31° C. Leben (17) reports a m.p. of 34° C.

When 4.2 gm. (0.025 mole) of 2-phenylpyridine-N-oxide was boiled with

30.7 gm. (0.20 mole) of phosphorus oxychloride for 30 min., the yield of 2-phenyl-4-chloropyridine picrate was 3.0 gm. (29%), and of 2-phenyl-6-chloropyridine 1.4 gm. (29%).

2-p-Anisylpyridine-N-oxide (*XIV; R = OCH_3*)

This compound was prepared in essentially the same manner as 2-phenylpyridine-N-oxide from the reaction of 30.5 gm. (0.165 mole) of 2-*p*-anisylpyridine with 0.275 mole of perbenzoic acid. A first crop of 17.0 gm. (51.5% yield) of the amine oxide, m.p. 132–136° C., and a second crop of 8.0 gm. (24%), m.p. 127–136° C., were obtained. Recrystallization from benzene gave white needles, m.p. 135–136° C. Calc. for $C_{12}H_{11}O_2N$: N, 6.97%. Found: N, 7.16 and 7.30%.

The *picrate* crystallized from methanol in long silky yellow needles, m.p. 136–138° C. Calc. for $C_{18}H_{14}O_9N_4$: N, 13.02%. Found: N, 13.10 and 13.31%.

Chlorination of 2-p-Anisylpyridine-N-oxide

Phosphorus oxychloride (24.5 gm.; 0.16 mole) was added to 4.0 gm. (0.02 mole) of 2-*p*-anisylpyridine-N-oxide. After standing for 10 min. at room temperature, the mixture was refluxed for 30 min. It was hydrolyzed with 200 gm. of cracked ice and made barely acid to Congo red. A pale tan solid, assumed to be 2-*p*-anisyl-6-chloropyridine (XV; R = OCH_3), melting at 87–100° C. was filtered off. It crystallized from methanol in pale tan flakes, m.p. 99–100° C. weighing 1.5 gm. (30% yield). A second crop (0.2 gm.; 4% yield) melted at 92–97° C. Calc. for $C_{12}H_{10}ONCl$: N, 6.38%. Found: N, 6.35%.

Both the aqueous and methanolic mother liquors of the solid, on being made strongly alkaline, became turbid. However, the compound which separated did not solidify on standing, and so was extracted with ether and treated with picric acid. A yellow solid, believed to be the *picrate of 2-p-anisyl-4-chloropyridine* (XVI; R = OCH_3) separated. It crystallized from methanol in tiny rods forming a feltlike mat, m.p. 167–168° C. The yield was 0.5 gm. (5%). Calc. for $C_{18}H_{13}O_8N_4Cl$; N, 12.48%. Found: N, 12.44%.

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NOTE

4-BROMOVERATROLE*

By R. A. B. Bannard and G. Latremouille

4-Bromoveratrole has been prepared in one step from veratrole bromination with air-diluted bromine vapor in glacial acetic acid (2), with bromine in carbon tetrachloride (4), and with N-bromosuccinimide in carbon tetrachloride (1). The latter method appeared to be the most desirable since the mild brominating action of the bromoimide should eliminate or minimize two disadvantages of the other methods, namely, demethylation and/or dibromination of the aryl ether. However, Buu-Hoï's procedure (1) was not entirely satisfactory because more than a 100% excess of veratrole had been used. The process was thereby made wasteful of veratrole and an unnecessary complication in isolation of the product introduced. The method was modified (*a*) by using equimolar quantities of reactants, and (*b*) by decreasing the volume of solvent relative to bromoimide. These modifications have increased the yield of 4-bromoveratrole to 83-86% of theoretical from 61% (1), as described in the experimental section. A small quantity of 4,5-dibromoveratrole (3) is formed as by-product.

Experimental

Sixty-nine gm. (0.50 mole) of veratrole (Eastman Kodak #274), 80 ml. of carbon tetrachloride (Merck Reagent), and 89 gm. (0.50 mole) of N-bromosuccinimide (Matheson #6123) were placed in a 500 ml. round-bottomed flask equipped with a reflux condenser protected by a calcium chloride drying-tube. The mixture was heated under reflux on the steam-bath for six hours and allowed to stand overnight at room temperature. The succinimide was separated from the deep red solution by suction filtration, using a medium porosity fritted-glass funnel, and washed with three 20 ml. portions of carbon tetrachloride. The carbon tetrachloride was removed from the combined filtrate and washings by distillation at atmospheric pressure. The residue was fractionated *in vacuo* yielding 93 gm. (86%) of 4-bromoveratrole as a colorless to pale yellow oil, b.p. 117-119.5° C. at 5 mm. (256.5° C. at 761 mm.); n_D^{20} 1.5722-1.5730. After distillation was complete and the system had cooled, a small quantity of pale yellow material crystallized on the upper walls of the still pot. A portion of this substance, on recrystallization from 95% ethanol, was identified as 4,5-dibromoveratrole by m.p. 88-90° C. alone and m.p. 90-92° C. in admixture with an authentic specimen of m.p. 91-92° C. (3).

Refractionation of a portion of the 4-bromoveratrole gave a colorless product, b.p. 116.5-117.5° C. at 4.5-5 mm.; n_D^{20} 1.5730; d_4^{20} 1.5068, 1.5069.

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Contents

Page

The Conductances of Aqueous Solutions of Sulphuric Acid at 50° and 75°—*A. N. Campbell, E. M. Kartzmark, D. Bisset, and M. E. Bednas* - 303

The Electrode Behavior of Mercury—*A. K. Wiebe and C. A. Winkler* 306

Silver – Silver Ion Exchange Reactions—*A. Baerg and C. A. Winkler* 319

The Use of Infrared Spectrophotometry for the Estimation of Small Quantities of Some Halogenated Hydrocarbons—*L. Breitman and E. W. R. Steacie* - - - - - - - - - - - - - - - - 328

Physicochemical Effects of Radio-frequency Fields—*H. H. Yates and C. A. Winkler* - - - - - - - - - - - - - - - - - 338

The Reactions of Active Nitrogen with Butenes—*H. Gesser, C. Luner, and C. A. Winkler* - - - - - - - - - - - - - - 346

Synthesis of Organic Deuterium Compounds. Part VI. Formaldehyde-d_2 and Formaldehyde-d—*R. A. B. Bannard, A. T. Morse, and L. C. Leitch* - - - - - - - - - - - - - - - - - - 351

A Kinetic Study of the Hydrolysis of Benzalaniline—*A. V. Willi and R. E. Robertson* - - - - - - - - - - - - - - - - 361

The Photolysis of Azoisopropane—*R. W. Durham and E. W. R. Steacie* - 377

Organic Deuterium Compounds. V. The Chlorination of Propyne and Propyne-d_4—*L. C. Leitch* - - - - - - - - - - - - 385

The Papilionaceous Alkaloids. XX. *Lupinus wyethii* S. Wats. and *Baptisia versicolor* Lodd.—*François Turcotte, Raymond Leduc, and Léo Marion* - - - - - - - - - - - - - - - - - - 387

Determination of the Neutron Capture Cross Section for the $Co^{59}(n, \gamma)Co^{60m}$ Reaction—*N. Moss and L. Yaffe* - - - - - - 391

Biochemistry of the Ustilaginales. VIII. The Structures and Configurations of the Ustilic Acids—*R. U. Lemieux* - - - - 396

The Kinetics of the Thermal Decomposition of Vinyl Isopropyl Ether—*Arthur T. Blades* - - - - - - - - - - - - - - - 418

The Electrolytic Polishing of Amphoteric Metals—*E. J. Casey and R. E. Bergeron* - - - - - - - - - - - - - - - - - 422

Dependence of Molecular Properties of Conjugated Compounds on the State of Electronic Excitation—*C. Sándorfy* - - - - 439

Betatron Irradiation of Water Saturated with Benzene—*G. R. Freeman, A. B. VanCleave, and J. W. T. Spinks* - - - - 448

Studies in the Preparation of Antimalarials from Pyridine—*Henry Gilman and John T. Edward* - - - - - - - - - - 457

4-Bromoveratrole—*R. A. B. Bannard and G. Latremouille* - - - 469

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